CATALYSIS

IN

ORGANIC CHEMISTRY

BY

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PREFACE

By his remarkable investigations on catalysis, Professor Sabatier has opened up new fields rich in scientific interest and fruitful in technical results. Catalytic hydrogenation will ever be an important chapter in chemistry. He is a teacher as well as an investigator and has done an important service in collecting from scattered sources a vast amount of information about catalysis and bringing the facts together in convenient and suggestive form in his book. I deem it a privilege to render his masterly work more accessible to English-speaking chemists.

The text and the unsigned footnotes represent Professor Sabatier's work as closely as I can make them. I have retained the characteristic italics. I have added a few notes which are signed by those responsible for them. In this connection I wish to thank my friends, among them Dr. Gibbs, Dr. Ittner, Dr. Adkins, and Dr. Richardson, for assistance, Professor Gomberg for verifying a number of Russian references, and Professor H. H. Lloyd for aid in proofreading.

To the chapter on the theory of catalysis, I have added an illuminating extension by Professor Bancroft, Chairman of the Committee on Catalysis of the National Research Council. In order to make the vast amount of detailed information in the book more readily available, I have prepared a subject index of some seven thousand entries and an author index of about eleven hundred names.

It is a pleasure to present a brief sketch of his life and abounding activities.

I have taken great pains to check the hundreds of references, but doubtless errors will be found. Corrections of any kind will be appreciated if sent me.

<div align="right">E. Emmet Reid.</div>

Johns Hopkins University,
Baltimore, Md.
August, 1921.

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PERIODICALS CITED AND THEIR ABBREVIATIONS

Am. Chem. J. *American Chemical Journal,* Baltimore.
Annalen. *Annalen der Chemie und Pharmacie (Liebig's),* Leipzig.
Ann. Chim. Phys. *Annales de chimie et de physique,* Paris.
Arch. Pharm. *Archiv der Pharmacie,* Berlin.
Berichte *Berichte der deutschen chemischen Gesellschaft,* Berlin.
Bull. Soc. Chim. *Bulletin de la Société chimique,* Paris.
Caoutchouc et G. *Caoutchouc et gutta-percha,* Paris.
C. A. *Chemical Abstracts,* Columbus.
C. or Chem. Centr. *Chemisches Centralblatt,* Leipzig.
Chem. News *Chemical News (The),* London.
Chem. Week. *Chemisch Weekblad,* Amsterdam.
Chem. Zeit. *Chemiker Zeitung,* Cöthen.
Compt. rend. *Comptes Rendus des Séances de l'Academie des Sciences de Paris,* Paris.
Dinglers *Dinglers Polytechnischer Journal,* Stuttgart.
Gas Light. *Gas Lighting,* London.
Gaz. Chim. Ital. *Gazetta chimica italiana,* Palermo.
Gaz *Le Gaz,* Paris.
Jahresb. *Jahresberichte über die Fortschritte der physischen Wissenschaften (von J. Berzelius),* Tübingen.
J. Am. Chem Soc. *Journal of the American Chemical Society,* Easton.
J. Chem. Ind. Tokio *Journal of Chemical Industry of Japan,* Tokio.
J. Ind. Eng. Chem. *Journal of Industrial and Engineering Chemistry,* New York.
J. Chem. Soc. *Journal of the Chemical Society,* London.
J. Gas Light. *Journal of Gas Lighting,* London.
Jour. Off. *Journal officiel de la République Française,* Paris.
J. Pharm. Chim. *Journal de Pharmacie et de Chimie,* Paris.
J. Phys. Chem. *Journal of Physical Chemistry,* Ithaca.
J. prakt. Chem. *Journal für praktische Chemie,* Leipzig.
J. Russ. Phys. Chem. Soc. *Journal of the Russian Physico-Chemical Society,* Petrograd.
J. Soc. Chem. Ind. *Journal of the Society of Chemical Industry,* London.
Lincei *Atti della Reale accademia dei Lincei,* Rome.
Mat. grasses *Matières grasses,* Paris.
Monatsh. *Monatshefte für Chemie,* Vienna.
Nachr. Ges. der Wiss. Göttingen *Nachrichten der königlichen Gesellschaft der Wissenschaften,* Göttingen.
Phil. Mag. *Philosophical Magazine,* London.
Proc. Roy. Soc. *Proceedings of the Royal Society,* London.
Pogg. Ann. *Annalen der Physik und Chemie (Poggendorf),* Leipzig.
Quart. J. Science *American Journal of Science,* New Haven.
Rec. Trav. Chim. Pays-Bas *Recueil des travaux chimiques des Pays-Bas,* Leyden.
Rev. Mois. *Revue du Mois,* Paris.
Rev. gen de chim. pure et app. *Revue générale de chimie pure et appliquée,* Paris.
Rev. Sci. *Revue Scientifique,* Paris.
Sitz. Akad. Wien. *Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse der kaiserlichen Akademie der Wissenschaften,* Vienna.

Seif. Zeit.   *Seifensieder Zeitung.*
Soc. Tech. Gaz.   *Société technique de l'Industrie gazière,* Paris.
Soc. Esp. Quim.   *Anales de la societad española de fisica y quimica,* Madrid.
Trans. Far. Soc.   *Transactions of the Faraday Society,* London.
Zeit. anorg. Chem.   *Zeitschrift für anorganische Chemie,* Hamburg.
Zeit. f. Chem.   *Kritische Zeitschrift für Chemie, Physik und Mathematik
     (Kekulé),* Heidelberg and Göttingen.
Zeit. Elektroch.   *Zeitschrift für Elektrochemie,* Halle.
Z. phys. Chem.   *Zeitschrift für physikalische Chemie,* Leipzig.

INTRODUCTION

PAUL SABATIER

PAUL SABATIER was born at Carcassonne Nov. 5, 1854. Admitted at the same time to the Polytechnic and the Normal School in 1874, he chose the latter from which he went out in 1877 receiving the highest grade in the competitive examination for *agregation de physique*.[1] After spending a year as Professor at the Lycée of Nîmes, he became, in October, 1878, assistant to Berthelot at the College de France. In July, 1880, he received the degree of Doctor of Science, his thesis being on Metallic Sulphides. After having been *Maître de Conférence* in physics in the Faculty of Sciences at Bordeaux for more than a year, he took charge, in January, 1882, of the course in physics in the Faculty of Sciences of Toulouse which he was never to leave. Taking charge of the chemistry course at the end of 1883, he was made Professor of Chemistry November 24, 1884, a position which he still occupies.

His chemical investigations are very numerous and touch various branches of that science: most of them have been published in the *Comptes Rendus de l'Academie des Sciences*, the *Bulletin de la Société Chimique,* and the *Annales de Chimie et de Phisique*.

His researches in physical chemistry stretch from 1879 to 1897 and comprise numerous thermochemical measurements (sulphides 1879–1881, chlorides 1889, chromates 1886, copper compounds 1896–1897, etc.), a thorough study of the velocity of transformation of metaphosphoric acid (1887–1889), studies on absorption spectra (1886 and 1894), on the partition of a base between two acids (1886–1887), etc.

In inorganic chemistry he has published numerous articles on metallic sulphides (1879–1880), the sulphides of boron and silicon (1880–1891), hydrogen disulphide (1886), the selenides of boron and silicon (1891), metallic chlorides (1881, 1894–1895), the chlorides (1881, 1888) and the bromide of copper (1896). A profound study of the oxides of nitrogen, which led to the characterization of metallic nitrides, was carried out (1897–1896) with the assistance of his pupil,

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[1] The *agregation* is a competitive examination which is considered extremely difficult.

J. B. Senderens. He prepared the deep blue nitrosodisulphonic acid (1896–1897), defined the tetracupric salts (1897), and obtained the basic mixed argento-cupric salts (1897–1899) which formed the starting point for a whole series of analogous compounds which Mailhe prepared subsequently.

His investigations in organic chemistry (starting in 1897) are the most important and include the general method of catalytic hydrogenation in contact with finely divided metals, which was awarded the Nobel prize for chemistry in 1912. The experiments involved in this as well as in the inverse dehydrogenation, were carried out with the aid of his successive pupils, J. B. Senderens (1899–1905), Alfonse Mailhe (1906–1919), Marcel Murat (1912–1914), Léo Espil (1914) and Georges Gaudion (1918–1919).

The study of metallic oxides as catalysts led Sabatier with Mailhe to discover a whole series of methods of transforming alcohols and phenols into mercaptans, amines, ethers, esters, etc., and also transforming acids (1906–1914). At the same time he carried out, either with Mailhe or Murat, a large number of syntheses of hydrocarbons and alcohols of the cyclohexane series, etc. (1904–1915).

In agricultural chemistry, Sabatier has published about fifteen memoirs on various subjects as well as *Lessons on Agricultural Chemistry*.

The Academy of Sciences of Paris awarded him the Lacaze prize in 1897 and the Jecker prize in 1905 and elected him correspondent of the chemical section in 1901, then non-resident *membre titulaire* in April, 1913. Awarded the Nobel Prize in Chemistry in 1912, Sabatier received in 1915 the Davy Medal of the Royal Society of London of which he was elected a foreign member in 1918. He is also a foreign member of the Royal Institution, the Academy of Sciences of Amsterdam, the Academy of Sciences of Madrid, the Royal Society of Bohemia, etc.

Profoundly attached to Toulouse, where he belonged to various local academies, Sabatier refused to leave his University to occupy the chair at the Sorbonne left vacant in 1907 by the death of Moissan. Dean of the Faculty of Sciences since 1905, he has created the three technical Institutes of Agriculture, of Chemistry and of Electrotechnique which are thronged by a large number of students.

CATALYSIS
IN ORGANIC CHEMISTRY

CHAPTER I

CATALYSIS IN GENERAL

1. By catalysis we designate the mechanism by virtue of which certain chemical reactions are caused, or accelerated, by substances which do not appear to take any part in the reactions.

A mixture of hydrogen and oxygen is stable at ordinary temperatures, but the introduction of a piece of *platinum black* causes immediate explosive combination; the platinum black is not visibly affected and can repeat the same effects indefinitely.

2. *Hydrogen peroxide* decomposes very slowly in cold water solution, a 30 volume solution requiring more than 240 hours at 17° for 50% decomposition, but the addition of 0.06 g. platinum black to 20 cc. of such a solution causes a vigorous evolution of oxygen and reduces the period of half decomposition to 8 seconds at 14°.[1] The platinum black, which does not seem to be altered, has by its presence enormously accelerated the reaction which normally takes place spontaneously but very slowly.

3. Substances which provoke or accelerate reactions without themselves being altered are called *catalysts*.

4. **History of Catalysis.** The first scientific observation of a catalytic transformation appears to be due to Kirchhof,[2] who, in 1811, showed that mineral acids, in hot water solution, change starch into dextrine and sugar, without being themselves altered by the reaction.

A short time afterwards, in 1817, Sir Humphrey Davy [3] observed that a slightly heated platinum spiral introduced into a mixture of air and a combustible gas, hydrogen, carbon monoxide, or hydrocyanic acid, becomes incandescent and causes the slow oxidation of

[1] LEMOINE, *Compt. rend.*, 162, 657 (1916).
[2] KIRCHHOF, *Schweigger's Jour.* 4, 108 (1812).
[3] DAVY, H., *Phil. Trans.*, 97, 45 (1817).

the gas. In 1820 Edmond Davy [4] discovered that platinum black can ignite alcohol with which it is wetted. Platinum sponge also possesses this power of provoking reactions without undergoing any appreciable change, and in 1831, Pelegrin Phillips,[5] a vinegar manufacturer of Bristol, took out an English patent on the use of platinum sponge to oxidise by air the sulphur dioxide obtained by roasting pyrites, thus producing sulphur trioxide. This was the germ of the contact process for the manufacture of sulphuric acid, which required the labors of half a century to render it industrially practicable.

In his masterful *Treatise on Chemistry*, Berzelius [6] discussed phenomena of this kind in which the presence of a material apparently having nothing to do with a reaction can yet cause that reaction to take place. Adopting a term which had been used in the seventeenth century by Libavius [7] with a different meaning, he grouped these phenomena under the designation *catalytic*, from the Greek κάτα, *down*, and λύω, *loose, I unloose.*

5. **Diversity in Catalysis.** The reactions in which catalysis is observed have multiplied with the advance of chemistry. They are extremely varied but can be divided into two distinct groups.

6. First we have catalysis in a homogeneous system, that is, where there is an intimate mixing of the various constituents, or at least between one of them and the catalyst that causes or accelerates the reaction. This is the case with the *soluble ferments* which are not considered in this treatise; it is also the case with *water vapor* in gaseous mixtures; with *iodine, sulphur* and various *metal chlorides* employed to aid chlorinations; with mineral acids in aldolization or crotonization as well as in the formation or saponification of esters; with alkalies in saponification; with *ferrous* or *manganous* salts in oxidations; with *zinc chloride* in the dehydration of alcohol; with *mercurous sulphate* in the sulphonation of aromatic compounds; with *anhydrous ether* in the preparation of organo-magnesium complexes; and even doubtless, in the Friedel and Crafts reaction with *aluminum chloride* which is partially soluble in the liquids used.

7. The second group is that of *heterogeneous systems* in which, for example, a solid catalyst is brought into contact with gaseous or liquid systems capable of reacting. It acts only by its surface, if it is compact and remains so during the reaction; by all its mass if it is

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[4] DAVY, E., *Schweigger's Jour.* **34**, 91 (1822); **38**, 321 (1823).

[5] *English patent* 6,069 of 1831.

[6] BERZELIUS, *Traité de Chemie*, I, 110 (1845).

[7] LIBAVIUS, *Alchemia*, Lib. II, vol. I, chapters XXXIX and XL, Frankfort, 1611.

porous, its surface then being extremely large as compared with its weight. The influence of the almost indefinite extension of the surface in the finely divided state is such that we are tempted to think of the catalytic activity of a material as belonging exclusively to that state (130).

8. Autocatalysis. Ostwald has designated by this term those reactions in which the products of the reactions accelerate the reactions.

Thus hydrogen and oxygen, rigorously dried, do not combine even at 1000°, but if the combination is once started, the water vapor so formed greatly favors the reaction, rendering it excessively rapid and explosive.

The decomposition of *hydrogen selenide,*[8] of *arsine*[9] and of *stibine*[10] are cases of autocatalysis, since the selenium, arsenic, and antimony set free accelerate the reactions when once they are started.

Pure nitric acid acts only slowly on many pure metals, silver, copper, bismuth, cadmium, and mercury, but when once started, the reaction accelerates itself because *nitrous fumes* are produced which facilitate the attack so that the reaction may become violent.[11]

We find further examples of autocatalysis in the spontaneous changes which certain organic nitro compounds undergo, *e. g.* powders with *nitrocellulose* as a base, such as powder B;[12] these changes produce acid vapors which accelerate the decomposition.

9. Negative Catalysts. Certain materials, when present in a chemical system, exercise an unfavorable or retarding influence; such are negative catalysts, the presence of which increases rather than decreases the chemical friction and may sometimes even paralyze the normal play of affinities.

10. For the present, it is convenient to place in this class substances capable of altering positive catalysts so as to diminish their efficient action.

As early as 1824, Turner[13] observed that traces of various substances suppressed the catalytic activity of finely divided platinum and mentioned as such ammonium sulphide, carbon disulphide, and hydrogen sulphide.

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[8] BODENSTEIN, *Zeit. physik. Chem.,* **29,** 428 (1899).

[9] COHEN, *Zeit. physik. Chem.,* **20,** 303 (1896).

[10] STOCK and GUTTMANN, *Berichte,* **37,** 901 (1904). BODENSTEIN, *Ibid,* p. 1361.

[11] VELEY, *Jour. Soc. Chem. Ind.,* **10,** 204 (1891).

[12] The French cannon powder which was used during the World War. It is pure nitrocellulose gelatinized by a mixture of 2 parts ether to 1 part alcohol.

[13] TURNER, *Pogg. Ann.,* **2,** 210 (1824).

In the manufacture of sulphuric acid by the contact process the presence of vapors of mercury, phosphorus, and particularly arsenic in the gas is sufficient to impair rapidly and destroy ultimately the catalytic action of the platinized asbestos.

In the use of finely divided nickel as a catalyst for direct hydrogenation, traces of chlorine, bromine, iodine, or sulphur compounds in the metal, in the hydrogen, or in the substance to be treated, suffice to prevent the reaction completely and somehow act as veritable poisons for the mineral ferment.[14]

Many other substances, without being toxic to the nickel, which they do not seem to injure, can retard the hydrogenation by their presence, e. g. glycerine, various organic acids, etc. Examples will be given in Chapter II (112 et seq.). In hydrogenations with nickel, the presence of small amounts of *carbon monoxide* in the hydrogen exercises a marked retarding influence.[15][16]

11. Negative catalysts, which by their presence, stabilize a chemical system and render its transformation more difficult, have been less studied than positive, but numerous examples may be given. It has long been known that hydrogen peroxide keeps better when slightly acid. The addition of a few hundredths of one per cent of sulphuric or hydrochloric acid to a 30 volume hydrogen peroxide considerably augments its stability. Thus at 65°, pure hydrogen peroxide required 3.2 hours for 50 per cent decomposition but this was increased to 35 hours by the addition of 0.026 molecule of hydrochloric acid.[17]

The spontaneous oxidation of chloroform to carbonyl chloride is hindered by the presence of a little alcohol.

Hydrocyanic acid is stabilized by traces of hydrochloric or sulphuric acid.[18]

In the oxidation of phenols by hydrogen peroxide in the presence of ferric chloride as catalyst, the reaction is retarded by the presence of mineral acids and even more by acetic, oxalic, and citric acids.[19]

The formation of the *organo-magnesium halides* in the Grignard reaction is retarded by the presence of *anisol, ethyl acetate, chloroform* or *carbon disulphide* (303).

[14] Sabatier, *Berichte*, **44**, 1984 (1911).

[15] Maxted, *Chem. News*, **117**, 73 (1918).

[16] Numerous quantitative experiments made by the translator in the Laboratory of Colgate and Company showed that catalytic nickel for hydrogenation is more injured, in use, by carbon monoxide than by any other catalyzer poison that is apt to be present.— E. E. R.

[17] Lemoine, *Compt. rend.*, **161**, 47 (1915).

[18] Liebig, *Annalen*, **18**, 70 (1836).

[19] Colin and Sénéchal, *Compt. rend.*, **153**, 76 (1911).

In the abstraction of halogens in the Wurtz or Fittig synthesis of hydrocarbons, *benzene* and *petroleum ether* exercise an unfavorable influence (605).

In the very complex reaction of the vulcanization of rubber, in which a large number of substances have a beneficial effect (104 and 107), phenyl-hydrazine is a very marked negative catalyst.[20]

12. Water which so often acts as a positive catalyst, can sometimes retard or even prevent reactions.

Moist hydrogen reduces nickel oxide less rapidly than dry.[21]

The decomposition of oxalic acid by hot concentrated sulphuric acid is impeded by the addition of very small amounts of water. The time of decomposition, under the same conditions of heating, is more than trebled by the addition of 0.05% of water, while 1% of sulphur trioxide renders the reaction tumultuous.[22]

The presence of a little water retards the decomposition of diazoacetic ester in alcoholic solution.[23]

Moisture retards the fixation of oxygen in the direct oxidation of unsaturated organic compounds in the presence of metallic catalysts.[24]

The presence of traces of water hinders the attack on metallic aluminum by fatty acids and by methyl, butyl, amyl, and benzyl alcohols as well as by various monophenols, ordinary phenol, the cresoles and α- and β-naphthols.[25]

13. In chemical systems in which *autocatalysis* takes place (8), the presence of substances which form stable compounds with the catalysts engendered during the reaction, hinders their effect. Hence such substances are *stabilizers*, or negative catalysts.

In the action of nitric acid on metals, various oxidising agents, hydrogen peroxide, potassium permanganate, and chloric acid are negative catalysts because they hinder the accumulation of nitrous fumes by oxidising them to nitric acid and thus preventing their action as positive catalysts.

With regard to powders having organic nitrates as bases (powder B, nitrogylcerine, etc.), all substances, such as amyl alcohol and diphenylamine, which are capable of fixing, either as salts or as esters, the acid products engendered by the slow spontaneous denitrification of such powders and which hasten their decomposition, are stabilizers.

[20] PEACHEY, *Jour. Soc. Chem. Ind.*, **36**, 424 (1917).

[21] SABATIER and ESPIL, *Compt. rend.*, **158**, 668 (1914).

[22] BREDIG and FRAENKEL, *Berichte*, **39**, 1756 (1906).

[23] MILLAR, *Zeit. physik. Chem.*, **85**, 129 (1913). BRAUNE, *Ibid.*, p. 170. SNETHLAGE, *Ibid.*, p. 211.

[24] FOKIN, *Zeit. anorg. Chem.*, **22**, 1451 (1909).

[25] SELIGMAN and WILLIAMS, *J. Soc. Chem. Ind.*, **37**, 159 (1918).

14. Inversion of Reactions. According to circumstances, catalysts are frequently able to work in inverse directions.

We have seen above (2) that platinum black thrown into hydrogen peroxide, induces its rapid decomposition with separation of oxygen. Inversely, platinum black serves to oxidise many substances, for example, alcohol which it transforms into aldehyde and acetic acid (244). It is now an oxidation catalyst and now a deoxidation catalyst.

15. At about 350°, hydrogen and iodine vapor combine rapidly in contact with platinum sponge,[26] and at the same temperature and with the same catalyst, hydrogen iodide is dissociated.[27]

Finely divided metals such as nickel reduced from the oxide, readily add hydrogen to hydrogenizable substances at 180°; benzene is thus transformed into cyclohexane (446). On the contrary, the inverse effect is produced when cyclohexane vapor is passed over nickel at 300°; hydrogen is eliminated and benzene is regenerated (641).

Reduced copper which is capable of hydrogenating aldehydes to alcohols at 180° (522), dehydrogenates alcohols at 250° to produce aldehydes (653).

The direct hydrogenation of nitriles over nickel at 180° readily furnishes primary amines (426); but inversely, nickel causes the decomposition of the amines at 350° into the nitriles and hydrogen (681).

Platinum, nickel, and copper are thus catalysts of hydrogenation or of dehydrogenation as the case may be.

16. Phenol vapor passed over thoria at 450°, is regularly dehydrated to form phenyl oxide (786); but the same catalyst at the same temperature can bring about the splitting of phenyl oxide by water to regenerate phenol.[28] Hence thoria is at the same time a catalyst for hydration and for dehydration.

17. It is the same way with strong mineral acids, such as sulphuric and hydrochloric, which are equally capable of bringing about the addition of water as in the saponification of esters (313), or its elimination as in esterification (749).

18. Soluble ferments, such as *emulsine,* which are in reality true catalysts, acting in homogeneous system, easily decompose glucosides by hydration and are also capable of synthesizing glucosides by dehydration. Thus *galactose* treated with emulsine in concen-

[26] CORENWINDER, *Ann. Chim. Phys.* (3), **34**, 77 (1852).

[27] HAUTEFEUILLE, *Compt. rend.,* **64**, 608 (1867).

[28] SABATIER, and ESPIL, *Bull. Soc. Chim.,* (4), **15**, 228 (1914).

trated solution condenses by dehydration into *galactobiose;* the latter, on the contrary, in dilute solution, is hydrated by the emulsine to regenerate the galactose.[29]

19. Reversible Reactions. In any reaction in which catalysts are able to activate the transformation in the two opposite directions, there results an equilibrium, the same limit being reached from either end. The catalyst only modifies the velocity of the opposing reactions without essentially changing their character; consequently in reversible reactions, the location of the limit is not, in general, changed by the intervention of the catalyst, though the catalyst enormously shortens the time required to reach that limit.

20. Lemoine has verified this for hydriodic acid which *immediately* reaches its limit of decomposition, 19% at 350°, in the presence of platinum sponge. Without a catalyst, at the same temperature, under 2 atmospheres pressure, the limit was 18.6% but was not reached till after 250 to 300 hours.[30]

21. Berthelot arrived at the same conclusions with the esterification of alcohols by acetic acid. For equivalent amounts of ethyl alcohol and acetic acid, the limit of 66.6% esterification is not attained at room temperature till after the lapse of several years of contact: on the contrary, in the presence of traces of hydrochloric or sulphuric acids, the identical limit is reached in a few hours.

22. An immediate consequence of the foregoing is that, in reversible reactions, the location of the limit is independent of the nature of the catalyst. This has been verified for the condensation of acetaldehyde. Whatever causes its polymerization into paraldehyde (hydrochloric acid, sulphur dioxide, oxalic acid, or zinc sulphate, etc.) always transforms the same proportion.[31]

23. Velocity of Catalyzed Reactions. The presence of a catalyst greatly influences the velocity of reactions. It is in order to examine the effect of:

1. Temperature,
2. Pressure,
3. Quantity of catalyst.

24. Temperature. Temperature plays a capital rôle in many catalytic reactions, just as it does in most chemical changes. They do not take place except above a certain temperature; the direct hydrogenation of benzene in the presence of nickel hardly takes place

[29] BOURQUELOT and AUBRY, *Compt. rend.,* **163**, 60 (1916).
[30] LEMOINE, *Ann. Chim. Phys.* (5), **12**, 145 (1877).
[31] TURBABA, *Zeit. physik. Chem.,* **38**, 505 (1901).

at all below 70°, while that of ethylene begins as low as 30° (413), and that of acetylene goes on at room temperature (423).

The decomposition of alcohol into ethylene and water by blue oxide of tungsten commences only at about 250° (709); the dehydration of phenol to phenyl oxide by thoria requires a temperature above 400° (786).

25. Elevation of the temperature also increases greatly the velocity of reactions: in fact it is found that, in a large number of cases, this velocity is doubled when the temperature is raised 10°. Reactions in which catalysts intervene do not escape the general rule and are greatly accelerated by elevation of temperature which is consequently favorable, so long as it does not greatly change the mechanism of the reaction — which, however, frequently happens. Thus catalytic hydrogenation is frequently replaced, above a certain temperature, by its reverse, catalytic dehydrogenation.

26. For example in the hydrogenation of benzene over nickel, the velocity of the formation of cyclohexane increases rapidly from 70°, where it is very slow, up to 180–200°, the most favorable temperature. From there on it decreases as 300° is approached, at which this reaction no longer takes place, cyclohexane being, on the contrary, decomposed into benzene and hydrogen or even into benzene and methane according to the equation:

$$3C_6H_{12} = 2C_6H_6 + 6CH_4,$$

this latter reaction becoming more important as the temperature is raised.[32]

27. In the hydrogenation of acetylene which takes place without complications at room temperature (423), elevation of temperature tends to introduce, by the side of the transformation into ethane, the condensation of acetylene into more complex molecules even to the formation of solid carbonaceous deposits (924).

28. In the dehydration of primary alcohols by contact with anhydrous oxides, elevation of temperature tends to introduce or to accelerate the reaction of dehydrogenation whereby aldehydes or compounds produced from them are formed (709).

29. Thus, by a judicious choice of reaction temperature, it is frequently possible to obtain, at will, various degrees of combination. For example, in the hydrogenation of anthracene over nickel, at 180°, perhydroanthracene, $C_{14}H_{24}$, is obtained along with the dodecahydro-; at 200° the octohydro- is prepared and at 260°, the tetrahydro-.[33]

[32] SABATIER, and SENDERENS, *Ann. Chim. Phys.* (8), 4, 334 (1905).

[33] GODCHOT, *Ann. Chim. Phys.* (8) 12, 468 (1907).

30. Pressure. Increase of pressure can scarcely have any considerable effect except in gaseous systems or in heterogeneous systems having a gaseous phase. In such cases, it can be foreseen that it will have a beneficial effect in those cases in which the number of molecules is diminished in the reaction.[34] This is the case in the hydrogenation of compounds containing an ethylene bond and practical use is made of it in the hydrogenation of liquid fats (956).

Likewise in the direct hydrogenation of phenol by nickel, in the liquid system around 150°, the formation of cyclohexanol is extremely slow in hydrogen at ordinary pressure, but, on the contrary, is rapid and complete under 15 atmospheres.[35]

31. On the contrary, molecular decompositions such as the dehydrogenation of alcohols into aldehydes or ketones, in contact with finely divided copper, are favored by a lowering of the pressure, which diminishes also the reverse reaction (653).

32. Quantity of Catalyst. We must at once distinguish between the two cases, whether the catalyst acts in homogeneous or heterogeneous systems.

In homogeneous systems, in which the catalyst remains in intimate mixture with the components of the reaction, it acts by its mass and its action increases with its concentration.

In the manufacture of sulphuric acid by the lead chamber process, in which oxides of nitrogen serve as the catalyst, the velocity is proportional to their concentration up to a certain limit.

In the inversion of sugar solutions by mineral acids (324), and in the saponification of esters by the same agents (313), the active agents in the catalysis are the free hydrogen ions arising from the electrolytic dissociation of the acids and the velocity of the reaction is proportional to the concentration of these ions.

In the catalytic decomposition of hydrogen peroxide by small amounts of alkali, the rapidity of the decomposition is nearly proportional to the concentration of the alkali.[36]

33. It is the same way with certain solid catalysts, iodine in the chlorination or organic compounds (278), and anhydrous aluminum chloride in the Friedel and Crafts reaction (883), which do not act till they have been dissolved in the liquids of the system to be transformed and then are comparable to liquid catalysts, with activity proportional to their concentration.

34. Heterogeneous systems are much more frequently met with:

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[34] Darzens, *Bull. Soc. Chim.* (4), **15**, 588 (1914).

[35] Brochet, *Ibid.* (4), **15**, 554 (1914).

[36] Lemoine, *Compt. rend.*, **161**, 47 (1915).

the catalyst in such is a solid phase in a liquid or gaseous medium and exercises its useful power only on its surface. The action, at first sight, depends on the extent of the surface, or at least on the mass of an extremely thin layer. A layer of silver 0.0002 mm. thick, deposited on glass, causes a very rapid decomposition of hydrogen peroxide.[37]

35. Solid catalysts are more active the greater their surface, and, for the same weight, the finer their grains; but there is, by no means, a rigorous proportionality between the activity and the extent of surface.

In liquids, convection currents which bring the material to be transformed into more or less perfect contact with the catalysts, have an important influence on the rate of the reaction, but one difficult to estimate. If the mixture is kept perfectly homogeneous, the active surface of a given catalyst, made up of grains of the same size, should be proportional to the number of grains, that is to say, to the total mass, but should increase very rapidly as the grains become smaller.

For a solid catalyst acting in a gaseous system, the incessant and very rapid movement of the gas particles is sufficient to assure the homogeneity of the system. The activity of the catalyst, if it is in a very thin layer, is proportional to the area of this layer. If the layer is thick, not only the surface particles act but also those within, the effect of the interior particles being more important, in proportion as the grains which compose the catalytic material are lighter and less agglomerated. With a solid in a fine powder, which is readily penetrated by the gas, the useful surface is extremely large as compared with the exterior surface of the layer. The state of division of a solid catalyst is a matter of prime importance. The catalytic power of nickel in sheets or even in thin foil is quite minute and of no practical value, while it is highly developed in the finely divided nickel which is obtained by reducing nickel oxide by hydrogen, below red heat, and particularly so when the oxide obtained by dehydration of nickel hydroxide is itself finely divided.

From this point of view, there are great differences in various catalysts according to the conditions of their preparation (see Chapter II).

[37] LEMOINE, *Ibid.*, **155**, 15 (1912).

CHAPTER II

ON CATALYSTS

36. As chemistry has developed, the number of catalytic phenomena has increased enormously and it has been recognized that the rôle of catalyst is played, not by a few bodies only but by a multitude of substances of every sort.

37. Solvents. The definition proposed by Ostwald, *" A catalyst is a substance which, without appearing in the final product, influences the velocity of a reaction,"* leads us to consider an infinite number of substances as catalysts. *Solvents,* whatever their nature, are catalysts since they do not appear in the equation of the reaction which they cause to take place.

In the absence of a liquid which dissolves them and thus realizes the contact which is indispensable to combination, solid substances which have no appreciable vapor pressure in the cold, are incapable of reacting with each other.

Dry crystals of oxalic acid and chromic anhydride can be mixed cold without any chemical change, but the addition of water which establishes perfect contact between the two substances, immediately starts the oxidation of the oxalic acid at the expense of the chromic anhydride. The water may be recovered completely and unchanged by the reaction. It acts as a catalyst.

38. The nature of the solvent can change greatly the velocity of reactions which take place in it, and furthermore, the influence which it exercises is absolutely special in each case.

Water is a true catalyst in the decomposition of hydrogen peroxide.[1]

In the fixation of hydrogen, by colloidal palladium, upon the acetylene triple bond, the solvent has an important influence of its own.[2]

The combination of *triethyl-amine* with *ethyl iodide* to form *tetraethyl-ammonium iodide* at 100°, is 203 times as rapid in *ethyl alcohol,* 718 times in *acetophenone,* and 742 times in *benzyl alcohol,* as it is in *hexane.*[3]

[1] LEMOINE, *Compt. rend.,* **155,** 9 (1912).

[2] ZAL'KIND and PISCHIKOV, *Jour. Russian Phys. Chem. Soc.,* **46,** 1527 (1914), *C. A.,* **9,** 2067.

[3] MENSCHUTKIN, *Zeit. phys. Chem.,* **1,** 611 (1887); **6,** 41 (1890).

39. In reversible reactions, the *limit* will not be altered by a change of solvent if this does not react in any way with either the reactants or the products: otherwise the limit will be modified. For example, in reactions between electrolytes, brought about in alcohol or in water, electrolytic dissociation is of great influence in case water is the solvent.

40. Solvents are not commonly classed with true catalysts as this designation is usually reserved for those substances which act in small concentration and of which a small quantity is able to cause large quantities of other materials to react.

DIVERSE SUBSTANCES CAN ACT AS CATALYSTS

41. The number of substances capable of acting as catalysts, is already very large and continues to increase with the progress of chemistry.

We find in this class the most varied materials: elements, oxides, mineral acids, bases, metallic chlorides, bromides, iodides, fluorides and oxygen salts, ammonia and its derivatives, and diverse organic compounds. But, particularly for solids, the catalytic activity can vary greatly according to their origin, either if they can exist in distinct molecular forms, or, more frequently, if they present themselves in different states of sub-division (32).

ELEMENTS AS CATALYSTS

42. Elements which are of themselves true catalysts, maintaining themselves unchanged during the course of the reactions which they provoke, are quite numerous and it is convenient to consider along with them those which pass immediately into compounds which act as catalysts. This is the case with chlorine, bromine, iodine, tellurium, sulphur, and phosphorus among the non-metals and tin, antimony, and thallium among the metals.

43. **Chlorine and Bromine.** These probably act by the immediate formation of the hydro-acids, to transform aldehydes into the polymeric paraldehydes.

44. **Iodine.** Iodine acts in the same way in the same reactions. It is frequently employed in chlorinations, and acts then by transforming itself into the *trichloride* which is the real factor in the catalysis. It permits the direct sulphuration of aromatic amines with the elimination of hydrogen sulphide (296). It can aid in causing

the condensation of aromatic amines with naphthols (790). It serves also to facilitate the reaction in the preparation of the organo-magnesium halides of the Grignard reagent, when it is desired to prepare these from chlorides or bromides (302).

45. Sulphur and Tellurium. Employed as carriers in chlorination, they certainly act in consequence of the initial formation of an equivalent amount of the chlorides. Tellurium has been proposed as an agent in direct oxidation (251).

46. Phosphorus. Red phosphorus has been mentioned as a catalyst for the dehydration of alcohols above 200° (699). The chief factor in this catalysis appears to us to be the small quantity of acids of phosphorus which exist in the phosphorus or which are produced from it by the oxidising effect of the alcohol.

47. Antimony, Tin and Thallium. Their use in chlorination is based on the primary formation of their perchlorides.

48. Carbon. All the porous forms of carbon have been employed as catalysts.

The carbonaceous mass obtained by calcining blood with potassium carbonate is a good catalyst for chlorination.[4]

Animal charcoal is a mediocre catalyst for the dehydration of alcohols (699), but is efficient in the preparation of carbonyl chloride from carbon monoxide and chlorine (282).

Coke may serve as an oxidation catalyst (258).

Wood charcoal, or baker's charcoal possesses considerable absorbing power for many gases, the consequence of which is frequently the production of special reactions. Carbon saturated with oxygen can produce oxidations: ethyl alcohol is changed to acetic acid. Ethylenic hydrocarbons are partially burned.[5]

Carbon saturated with chlorine enables us to chlorinate sulphur dioxide in the cold as well as hydrogen.[6]

Baker's charcoal catalyzes the decomposition of primary alcohols above 380°, giving, at the same time, aldehydes and ethylene hydrocarbons (679). It is frequently employed for the preparation of carbonyl chloride (282).

49. The porosity of the carbon has a great influence. Thus in the case of 30 volume hydrogen peroxide of which the half decomposition at 17° required 240 hours, the addition of 5% of cocoanut charcoal (in pieces 1 to 2 mm. in size) reduced this time to 15.4 hours, while the same weight of charcoal from the black alder lowered it

[4] DAMOISEAU, *Compt. rend.,* **83,** 60 (1876).
[5] CALVERT, *Ibid.,* **64,** 1246 (1867).
[6] MELSENS, *Ibid.,* **76,** 92 (1873).

only to 212 hours. *Sugar charcoal* falls between these two as an activator.[7]

50. **Sodium** brings about the isomerization of unsaturated hydrocarbons, *e. g., diethylallene* into *diethylallylene* (192). It polymerizes *isoprene* (213) as well as *acetonitrile* (231).

51. **Magnesium.** Magnesium powder has been mentioned as very active in decomposing hydrocarbons at 600° (918).

Aluminum. The same property has been claimed for aluminum which has been proposed as a chlorination catalyst also because it changes immediately to the chloride. Aluminum turnings are only a mediocre catalyst for oxidation (255).

52. **Manganese.** Powdered manganese is a poor catalyst for oxidations (255) but is an excellent aid to bromination (292).

Zinc turnings, at 100°, can cause the condensation of acetaldehyde into aldol or into crotonic aldehyde (219). The same metal acts as a dehydrogenating agent on alcohols at 600–50°, temperatures at which the metal is melted, a condition unfavorable to catalytic action (670).

53. **Nickel.** Employed in the state of extremely fine division, as is obtained by the reduction of the oxides by hydrogen or carbon monoxide, nickel is a marvelous catalyst, the manifold activity of which has been established by the investigations of Sabatier and Senderens, beginning in 1879. It is specially suitable for the direct hydrogenation of volatile organic compounds, but it is equally capable of producing dehydrogenations and decompositions whether they are followed by molecular condensations or not. Chapters VIII, IX and XII are devoted to catalytic reactions effected by nickel.

54. The metal in sheet or even in thin foil possesses only slight activity. Catalytic nickel should be prepared by reducing the oxide, and as the metal so produced is readily oxidised and frequently pyrophoric, it is generally best to carry out the reduction in the same tube in which the catalysis is to be effected. However this is not absolutely necessary, if the precaution is taken to cool the reduced metal perfectly in the current of hydrogen, or better still in a current of pure nitrogen.[8] The metal so prepared can be preserved in a well-

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[7] LEMOINE, *Ibid.*, 162, 725 (1916).

[8] When freshly prepared highly active nickel is exposed freely to the air, a rapid heating takes place that considerably impairs its catalytic activity. The change which takes place in the nickel is brought about and augmented by the heat produced by the catalytic oxidation of the hydrogen occluded and surrounding the nickel when it comes in contact with an excess of oxygen from the air. Similar oxidation of hydrogen is well known in the presence of catalytic palladium or platinum. In the case of catalytic nickel, however, the heat thus

stoppered bottle for quite a long time without considerable alteration.

55. The activity of the reduced nickel varies greatly according to the nature of the oxide and the manner of reduction. The metal is more active, the greater its surface; and the lighter the oxide and the lower the reduction temperature, the greater is this surface.

Nickel reduced at a bright red is no longer pyrophoric and possesses a considerably reduced catalytic power.

On the contrary, that which comes from the hydroxide precipitated from the nitrate, dried and reduced around 250°, has an excessive activity along with maximum alterability. It can be compared to a spirited horse, delicate, difficult to control, and incapable of sustained work.

Applied to phenol, it passes by cyclohexanol and produces cyclohexane to a large extent. It tends to produce molecular dislocations in bodies submitted to catalysis.

56. An excellent quality of nickel is obtained by dissolving the commercial cubes in pure nitric acid (free from hydrochloric), calcining the nitrate at a dull red and reducing at about 300° the oxide thus obtained. Such a nickel can do all kinds of work and maintains its activity for a long time.

It has been stated that nickel prepared above 350° is incapable of hydrogenating the aromatic nucleus,[9] but Sabatier and Espil have shown that this ability is still possessed by a nickel prepared at 700° even when it is kept at this temperature for several hours, but not by nickel prepared by reduction above 750° or heated for some time at 750°.[10]

57. **Cobalt.** Finely divided cobalt, such as is obtained by the reduction of the oxide by hydrogen, can be employed as a catalyst for the same purposes as nickel, but is less useful as it is less active,

generated in the presence of an excess of oxygen, or air, produces an oxidation of the catalyzer to an extent that lessens or destroys its activity. A number of experiments were made in which freshly prepared nickel catalyzer still in the presence of hydrogen was subjected to the action of a Geryk pump which exhausted practically all of the excess hydrogen gas. In different experiments the catalyzer was then, while cold, allowed slowly to come in contact with carbon dioxide, nitrogen, and air. The catalyzers so formed were active and retained their activity reasonably well. In case air was admitted to the vacuum vessel containing the catalyzer, it was introduced very slowly so that any oxidation would be so slight as not to increase the temperature sufficiently to produce cumulative oxidation. — M. H. ITTNER.

[9] DARZENS, *Compt. rend.*, **139**, 869 (1904); BRUNEL, *Ann. Chim. Phys.* (8), **6**, 205 (1903).

[10] SABATIER and EPSIL, *Bull. Soc. Chim.* (4), **15**, 779 (1914).

and as the reduction of its oxide requires a higher temperature, in fact above 400°.

58. Iron. Reduced iron can replace nickel in quite a large number of cases, but disadvantages, like those mentioned for cobalt, are more serious, the oxides being still more difficult to reduce. Between 400° and 450°, it is necessary to prolong the action of the hydrogen for six or seven hours to obtain complete reduction. Furthermore, the metal reduced at this high temperature is no longer pyrophoric and retains only mediocre activity. However, pulverized iron is a useful catalyst for decompositions accomplished at a low red heat (932).

Iron has been mentioned as a chlorination catalyst, but in that case it serves only to form iron chloride which is the real catalyst.

59. Copper. Copper, reduced from its oxide by hydrogen, constitutes, on account of its ease of preparation, the low temperature at which the oxide can be reduced, below 180°, and the regularity of its action, a valuable catalyst for certain reactions, but it is not capable of effecting all kinds. Its activity also varies considerably according to the method of production. The black oxide of copper, prepared by roasting the metal or by calcining the nitrate at a bright red, furnishes by reduction, with incandescence, a clear red, very compact metal with low catalytic power. By reducing with a slow current of hydrogen (to avoid incandescence) at about 200°, the *tetracupric* hydroxide — such as is precipitated from boiling cupric salt solutions by alkalies — a very light violet colored metal is obtained with much greater catalytic activity. The very fine copper powder which is commercially prepared for imitation gilding, can frequently be used: it is only necessary to free it from grease by washing with ether or ligroine.

This latter has been used to facilitate several of the reactions of aromatic diazonium salts in which nitrogen is eliminated (606). It is efficient in causing the production of phenyl oxide by the action of brombenzene on sodium phenylate (904).

Copper in spirals, or in gauze, has been employed, with advantage, in the catalytic oxidation of alcohols, ethers, hydrocarbons, and amines (254).

60. Silver. Silver powder is an excellent oxidation catalyst (253). Inversely, it causes the rapid decomposition of hydrogen peroxide, transforming itself into the oxide Ag_4O_3 which continues the catalysis.[11]

61. Platinum. Platinum is one of the longest known catalysts.

[11] BERTHELOT, *Bull. Soc. Chim.* (2), **34**, 135 (1880).

Not oxidisable in the air at any temperature, it is a powerful catalyst for oxidation or for hydrogenation, especially when it is finely divided and presents a large surface. This is the condition realized in platinum *sponge*, a porous material obtained by calcining ammonium chlorplatinate, and even better in *platinum black* and in *colloidal platinum*, which can be mixed intimately with liquids submitted to catalysis (67).

62. **Platinum black** can be prepared either by reducing acid solutions of platinic chloride [12] by zinc, or better by magnesium, or by treating the platinum chloride with alcohol and alkalies,[13] or by reducing the platinum salt with sodium formate,[14] or with sodium tartrate, or even with glucose in alkaline solution, or by glycerine and potash.[15]

An excellent method is that of Loew: 35 cc. formalin is added to 25 g. platinum chloride dissolved in 30 cc. water and then, little by little, while cooling 25 g. caustic soda dissolved in its own weight of water. After twelve hours it is filtered off and washed. A spongy mass is thus obtained which is dried in the cold over sulphuric acid.[16]

Platinum black always retains traces of substances with which it has been in contact during its preparation. Blacks prepared in alkaline solution are more active than those from acid solution.

63. According to Lemoine the grains of platinum black, of which the diameter is about 0.1 mm., are much more active than those of the sponge for the same area. With a specimen of hydrogen peroxide which, without catalyst, required ten days for half decomposition, this time was reduced by platinum black to 0.00013 hour and with the same surface of the sponge only to 0.2 hour. The black possesses a specific activity which is, without doubt, due to less molecular condensation and which disappears when it is heated to 400 to 500°.[17]

This weakening by heating is progressive. Thus platinum black is not sensibly altered as a hydrogenation catalyst when heated below 300° and still retains its power to transform limonene into menthane by the fixation of $2H_2$. If it is heated to 430°, it is considerably weakened and can add only H_2 to the external double bond, giving carvomenthene. Heated to 500°, it loses all activity.[18]

[12] BOETTGER, *J. Prakt. Chem.* (2), **2**, 137 (1870).

[13] ZEISE, *Pogg. Ann.*, **9**, 632 (1827).

[14] DOEBEREINER, *Ibid.*, **28**, 181 (1833).

[15] ZDRAWKOWITCH, *Bull. Soc. Chim.* (2), **25**, 198 (1876).

[16] LOEW, *Berichte*, **23**, 289 (1890). Improved directions for this important preparation are given by WILLSTÄTTER and WALDSCHMIDT-LEITZ in *Berichte*, **54**, 121 (1921).—E. E. R.

[17] LEMOINE, *Compt. rend.*, **162**, 657 (1916).

[18] VAVON, *Ibid.*, **158**, 409 (1914).

Compact platinum in foil or wire has a certain activity, at least, if it has been previously heated above 50°. A heated platinum spiral introduced into a mixture of alcohol vapor and air or oxygen, causes the formation of aldehyde and the incandescence which results from the heat liberated in the oxidation, maintains itself indefinitely so long as the mixture is renewed: this is the *lamp without flame*.[19]

64. Rhodium, Ruthenium, Iridium, and Osmium. Employed in the form of the pulverulent black, or as sponge, these metals act in the same manner as platinum, at least as regards reactions of oxidation or of decomposition, but they are less active in hydrogenation (580).

Rhodium or iridium black decomposes, in the cold, formic acid into hydrogen and carbon dioxide (822). In contact with alcohol and caustic soda, hydrogen is evolved with the formation of sodium acetate.[20]

65. Palladium. Palladium exhibits the property of absorbing very large quantities of hydrogen, even up to 930 times its own volume.[21] Palladium thus saturated with hydrogen can effect a large number of hydrogenations. But the metal can serve also as a temporary support for hydrogen, that is to say, as a hydrogenation catalyst, in the form of sponge or black (573), and can be employed as a catalyst for dehydrogenation (669), for decomposition (624), or for polymerization (212).

66. Gold. Gold, when finely divided, has catalytic properties resembling those of silver.

67. Colloidal metals. The catalytic activity of metals, being in direct relation to the extent of their surfaces, consequently to the minuteness of their particles, should reach its maximum in the colloidal state. As the chemical alterability of the metals is also intensified by their extreme subdivision, it would hardly be expected that any could be practically used in this state except those *not oxidisable in the cold*, such as platinum, palladium, gold and silver.

68. Bredig[22] has described a simple method for preparing colloidal metals: an electric arc is made to play between two wires of the metal under pure water. A sort of nebulosity is observed which becomes darker and darker till it is soon so opaque that the spark

[19] HOFMANN, *Annalen*, 145, 358 (1868).

[20] SAINTE-CLAIRE-DEVILLE and DEBRAY, *Compt. rend.*, 78, 1782 (1874).

[21] GRAHAM, *Phil. Mag.*, (4), 32, 401 and 503 (1866); 36, 63 (1868). *Proc. Roy. Soc.*, 15, 223, 502 (1867); 16, 429 (1868); 17, 212 and 500 (1869). *Compt. rend.*, 63, 471 (1866) and 68, 101 (1869).

[22] BREDIG, *Zeit. physik. Chem.*, 31, 258 (1899); 37, 1, 323 (1901); *Berichte*, 37, 798 (1904); *Zeit.* Elektroch., 14, 51 (1908).

can not be seen. Solutions thus obtained can be preserved for a long time and contain 0.09 to 0.02 g. gold per liter and a less amount of palladium or platinum: the number of particles in such a solution may reach as high as a billion per cubic millimeter.

69. Unfortunately such solutions are unstable in the presence of various substances. The presence of suitable organic materials gives them stability and Paal has found that egg albumen has this effect. He dissolves 15 parts of caustic soda in 500 parts of water, adds 100 parts egg albumen and warms on the water bath till solution is nearly complete. It is acidulated with sulphuric acid and the precipitate filtered off. The solution is neutralized with soda, evaporated on the water bath to a small volume and again acidulated with sulphuric acid.

The filtered solution is dialyzed to separate the sodium sulphate. The liquid remaining in the dialyzer is treated warm with baryta water which precipitates the remaining sulphate ions. The filtered solution is evaporated on the water bath and several volumes of alcohol added, which precipitates white flakes which Paal has named *lysalbinic acid.* When dry, this is a white powder, soluble in water and nearly insoluble in alcohol: its weight is about one-fourth that of the albumen.

One gram of the above product is dissolved in 30 cc. water and made alkaline with a slight excess of soda, 2 g. platinum chloride dissolved in a little water is added and then a slight excess of *hydrazine hydrate.* The solution turns dark and a gas is evolved: after five hours it is dialyzed to eliminate electrolytes, carefully evaporated on the water bath and dried in vacuum. Brilliant black scales are obtained which dissolve in water to form a black opaque solution: this is *colloidal platinum.*

Colloidal palladium is prepared in an analogous manner.[23]

Solutions of these are very stable and can even be heated for a long time without change.

70. In this way colloidal solutions can be prepared of silver, gold, copper, osmium, and iridium, all decomposing hydrogen peroxide with extreme energy. Traces of osmium produce this effect.[24]

71. Skita prepared a colloidal palladium hydroxide, for use as a hydrogenation catalyst, by heating to boiling a solution of palladium chloride, $PdCl_2$, with soda and a little gum arabic. The solution is

[23] Paal, *Berichte,* 35, 2195 (1902). Paal and Amberger, *Ibid.,* 37, 126 (1904) and 38, 1398 (1905). Kelber and Schwartz, *Ibid.,* 45, 1946 (1912). Skita and Meyer, *Ibid.,* 45, 3579 (1912).

[24] Paal and Amberger, *Berichte,* 40, 2201 (1907). Paal, Biehler and Steyer, *Ibid.,* 50, 722 (1917).

dialyzed till neither silver nitrate nor baryta water gives a test outside. The solution, evaporated to dryness in a vacuum, gives brown scales of colloidal palladium hydroxide, insoluble in cold water but soluble in water containing traces of acid or alkali.

Another method of preparing colloidal palladium, given by the same author, is to pass a current of hydrogen through a warm solution of palladous chloride and gum arabic.

A colloidal platinum hydroxide, analogous to that of palladium, is obtained by treating a boiling solution of potassium chlorplatinate with the theoretical amount of decinormal soda and adding gum arabic. The brown solution by dialysis, and evaporation in vacuum, gives a black solid, insoluble in water but made soluble by a trace of alkali.

The solutions so obtained can be neutralized, dialyzed and evaporated in vacuum: the black scales so obtained dissolve readily in water and can be employed for hydrogenations in acid media (561). The solutions are not coagulated by boiling with acetic acid, nor by heating with water under pressure.

In another process, called the *germ method*, the same chemist adds to a solution of platinum chloride, $PtCl_4$, containing gum arabic, a trace of a previously prepared colloidal platinum in solution, and submits the liquid to the action of compressed hydrogen, by which means a colloidal solution of the metal is obtained.[25]

72. Among colloidal metals, the maximum activity for oxidations belongs to platinum, osmium being only slightly active:[26] for hydrogenations, silver and osmium are much inferior to platinum and particularly to palladium; gold and copper produce no effect.[27]

OXIDES AS CATALYSTS

73. **Water.** Water appears frequently as a positive catalyst: quite a large number of reactions are not readily carried out except in the presence of traces of moisture. Oxidations are generally more difficult to realize by means of oxygen rigorously dried.[28] A mixture of absolutely dry carbon monoxide and oxygen can not be made to explode. A flame of carbon monoxide is extinguished in perfectly dry air.[29] Carbon and even phosphorus refuse to burn in perfectly

[25] Skita, *Berichte,* **45,** 3312 (1912).

[26] Paal, *Berichte,* **49,** 548 (1916).

[27] Paal and Gerum, *Berichte,* **40,** 2209 (1907).

[28] Dixon, *Proc. Roy. Soc.,* **37,** 56 (1884).

[29] Traube, *Berichte,* **18,** 1890 (1885).

dry oxygen.[30] Hydrogen and oxygen thoroughly dried do not combine up to 1000°. Ammonia and hydrogen chloride when rigorously freed from moisture do not form any solid ammonium chloride and, conversely, thoroughly dry ammonium chloride can be volatilized without decomposition and the density of its vapor is then normal.[31]

A trace of moisture is sufficient to cause the transformation of vitreous arsenic trioxide into its octahedral isomer (porcelain like).[32]

Absolutely dry fluorine does not attack glass (Moissan).

This beneficial catalytic effect of water is quite exceptional in organic reactions, but we may mention that in the catalytic oxidation of methyl alcohol vapors by a platinum spiral, the presence of water favors the production of formaldehyde. With absolute methyl alcohol, incandescence is not produced unless the spiral has an initial temperature of at least 400°, while with 20% of water in the alcohol, 175° is sufficient.[33]

74. Sulphur Dioxide. Small amounts of this gas are sufficient to cause the polymerization of acetaldehyde into paraldehyde or metaldehyde (482).

75. Anhydrous Metallic Oxides. Manganese dioxide rapidly decomposes hydrogen peroxide, without itself being altered. The same is true of the yellow oxide of lead in alkaline solution. Cuprous oxide is an active catalyst for the decomposition of diazonium salts (606).

The studies that have been made in commercializing the contact process for sulphuric acid, discovered in 1831 (4), have shown that various finely divided metallic oxides may be substituted for the platinum. As early as 1852, Wöhler and Mahla suggested for this purpose, oxides of iron, chromium and copper; and Pétrie, Plattner, and Reich advised the use of pulverized silica.[34] In 1854, Tornthwaite proposed manganese oxide.

The application of anhydrous metallic oxides to the catalytic oxidation of volatile organic compounds was proposed anew in 1906 by Sabatier and Mailhe, who mentioned specially the oxides of copper, nickel, cobalt, chromium, manganese and uranium (260). Matignon and Trannoy made the same suggestion (260).

Several anhydrous metallic oxides, particularly alumina, thoria, blue oxide of tungsten, titania and zirconia, etc., are endowed with

[30] Baker, *J. Chem. Soc.*, **47**, 349 (1886).

[31] Baker, *Ibid.*, **65**, 611 (1894).

[32] Winkler, *J. pr. Chem.* (2), **31**, 247 (1885).

[33] Trillat, *Bull. Soc. Chim.*, (3), **29**, 35 (1903).

[34] Silica gel has been found by Patrick to be an excellent catalyst for the oxidation of nitric oxide by oxygen. — E. E. R.

important catalytic activity towards alcohols, which they can decompose into unsaturated hydrocarbons (701). They can catalyze the synthesis of thiols (743), amines (732), ethers or phenol ethers (786 and 789) and esters (762). These oxides and manganese oxide, employed as catalysts with acids produce symmetrical ketones (837), mixed ketones (847), aldehydes (851) and decompose esters (858). They can also bring about the isomerization or polymerization of unsaturated hydrocarbons (211).

76. The catalytic power of these various oxides is very variable, according to the method of preparation.

Catalysis being a matter of surface, the amorphous oxides prepared from precipitated hydroxides, dehydrated at low temperatures, are much more active than crystallized oxides or those that have been sintered together by calcination at a red heat.

These latter possess, for equal mass, a much smaller surface and are frequently, without doubt, in an advanced stage of molecular condensation. This is particularly true of the oxides of the metals of small atomic weight, aluminum, iron, silicon, chromium, etc. The action of acids has long shown such differences.

77. Amorphous *alumina,* obtained by dehydrating the hydroxide below 400°, dissolves readily in mineral acids and is an active catalyst for alcohols, while crystallized alumina and amorphous alumina calcined at a bright red, are insoluble in acids and have almost no catalytic power for alcohols.

Analogous differences are observed with the different varieties of *silica,* though, for the decomposition of hydrogen peroxide, silica calcined at red heat is more active than the dried silica.[35]

Ferric oxide prepared by dehydrating the precipitated hydroxide below 350°, is a much more powerful catalyst for alcohols than that obtained at a red heat.[36]

It is the same with regard to hydrogen peroxide of which the former decomposes 50% in 10 seconds, while the latter requires 1550 seconds.

78. Furthermore, the very nature of the catalyst is modified by these changes of constitution of the oxides.

The *sesquioxide of chromium,* prepared by dehydrating the blue precipitated hydroxide, gives with ethyl alcohol 4.2 cc. gas per minute containing 91% of ethylene, while, after calcination at 500°, the same oxide furnishes only 2.8 cc. gas with 40% ethylene. The oxide pre-

[35] LEMOINE, *Compt. rend.,* 162, 702 (1916).

[36] SABATIER and MAILHE, *Ann. Chim. Phys.,* (8), 20, 313 (1910).

pared by the explosion of ammonium bichromate and, consequently formed with incandescence, gives 1.2 cc. gas, with 38% ethylene.[37]

The crystallized oxide gives no gas at all at 350°, and 400° must be reached to obtain 2 cc. which is then nearly pure hydrogen. The catalytic function is modified at the same time that it is weakened.[38]

Analogous variations have been observed with *silica* and *alumina*, both in the intensity and in the direction of the decomposition,[39] and a relation has been noted between the catalytic activity of alumina and its solubility in acids.[40]

79. **Thoria,** on the contrary, does not present this inconvenience and its activity is not sensibly diminished when it is calcined at a red heat: it appears that such a heavy molecule can not suffer important polymolecular condensations.

80. **Nickel oxide** and especially **nickel suboxide,** which results from the incomplete reduction of the monoxide, have been regarded by some chemists as the best catalysts for carrying out the hydrogenation of organic compounds in a liquid medium. At least as active as reduced nickel, they have the advantage of being less alterable and consequently of retaining their catalytic activity longer (584). The researches of Sabatier and Espil have indeed established the existence of a suboxide, apparently Ni_4O, which is the first step in the reduction of the monoxide, but they have shown that this suboxide, while it is being formed, is partially reduced to the metal and it is this latter which is the sole factor in the hydrogenations that have been attributed to the oxide.[41]

The same reservations should be applied to the *oxide* of *osmium*, which has been proposed as a hydrogenation catalyst (583) and which, doubtless, serves only as a source of finely divided osmium.[42]

MINERAL ACIDS

81. Strong mineral acids frequently act as catalysts in chemical reactions.

Hydrochloric and *sulphuric acids,* employed in small amounts, bring about the rapid esterification of alcohols by organic acids (749). Hydrochloric acid shows itself also efficacious for the production of acetals from alcohols (782) as well as of similar compounds from

[37] LEMOINE, *Compt. rend.,* **162,** 702 (1916).
[38] SABATIER and MAILHE, *Ann. Chim. Phys.,* (8), **20,** 339 (1910).
[39] SENDERENS, *Bull. Soc. Chim.,* (4), **3,** 823 (1908).
[40] IPATIEF, *Berichte,* **37,** 2986 (1904).
[41] SABATIER and ESPIL, *Compt. rend.,* **158,** 668 (1914) and **159,** 140 (1914).
[42] NORMANN and SCHICK, *Arch. Pharm.,* **252,** 208 (1914), *C. A.,* **8,** 3129.

glucose with alcohols and thiols.[43]   It also causes catalytic dehydrations in the condensation of ketones (795) and in analogous reactions.

Sulphuric acid behaves similarly in the *crotonization* of aldehydes and in similar condensations.

These two acids intervene in a similar manner in the acetylation of amines, *e. g.* of urea. Acetanhydride, without catalyst, gives a yield of only 19.3%, but 73.3% with one molecule of hydrochloric acid, and 61% with one molecule of sulphuric acid.[44]

82. But these acids more frequently accomplish the reverse catalysis in causing hydrolysis, or decomposition by addition of water, and this aptitude they have in common with all *strong* soluble *mineral acids,* because it is in consequence of their ionization and should be considered as due to the *hydrogen* ions which they furnish. Their hydrolytic activity is proportional to their electrolytic dissociation.

We have cases of this decomposition by the addition of water, in the various catalytic effects of acids in the saponification of esters and fats (314), the hydrolysis of amides (331), of anilides, of certain aromatic sulphonic acids,[45] of acetals, in the inversion of sucrose, and, in a more general manner, in the decomposition of polysaccharides such as starch and dextrine.

Hydrochloric acid is a very active polymerizing catalyst for aldehydes, whether it produces a simple *aldolization* with conservation of the aldehyde function (219), or a cyclization into molecules more or less condensed such as paraldehyde (222).

Sulphuric acid, in small amounts, can likewise cause the change of acetaldehyde into paraldehyde and also the polymerization of ethylene hydrocarbons (210).

Hydriodic acid, in its capacity of a strong acid, can effect hydrolyses, as do the above acids. We may mention also its use in facilitating the preparation of the mixed organo-magnesium halides from chlorides in the Grignard reaction (302).

Nitrous acid catalyzes the transformation of oleïc acid into its isomer, elaïdic acid (186).

INORGANIC BASES

83. The alkalies, and alkaline earths, caustic potash and soda, baryta and lime, frequently act as catalysts. In inorganic chemistry they cause the rapid decomposition of hydrogen peroxide and hydrogen persulphides.

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[43] EMIL FISCHER, *Berichte,* **26,** 2400 (1893) and **27,** 615 (1894).

[44] BÖESEKEN, *Rec. Trav. Chim. Pays-Bas,* **29,** 330 (1910).

[45] CRAFTS, *Berichte,* **34,** 1350 (1901).

In water solution, these strong bases, being highly ionized, *hydrolyze esters* rapidly. Saponification, when carried out in the presence of excess of alkali, appears, at first sight, to be simply the consequence of the formation of the alkali salt of the acid of the ester, but, in reality, the phenomenon consists of two successive phases, first the hydrolysis which liberates the acid and then the neutralization of the acid to form the salt.

Solutions of *lime* bring about rapid aldolization of aldehydes (221).

A mixture of formaldehyde and acetaldehyde, on long contact with *milk of lime*, engenders a tetraprimary erythrol along with formic acid.[46]

Solid caustic potash causes the aldolization of acetaldehyde and alcoholic potash, the polymerization of isobutyric aldehyde (224).

Caustic alkalies frequently produce isomerizations (185).

FLUORIDES, CHLORIDES, BROMIDES, AND IODIDES

84. Boron Fluoride. Among fluorides, that of boron merits special mention. It produces polymerizations of hydrocarbons: one part of it is sufficient to polymerize 160 parts of oil of turpentine.[47]

85. Iodine Chloride. The trichloride ICl_3, the immediate product of the action of excess of chlorine on iodine, is a valuable agent in the direct chlorination of organic compounds by gaseous chlorine (278).

86. Barium Chloride. The anhydrous salt readily causes the decomposition of alkyl chlorides into hydrochloric acid and the ethylene hydrocarbons (876).

87. Aluminum Chloride. The anhydrous chloride is a catalyst of immense value. It can be employed as an agent in direct chlorination or bromination (284 and 293).

It causes the direct fixation on benzene, of oxygen (263), of sulphur (296), and of sulphur dioxide (297).

It can bring about the decomposition of alkyl chlorides (877) and of thiophenol (297).

In the acetylation of urea it is a much more active catalyst than hydrochloric acid.[48]

Anhydrous aluminum chloride is the basis of a very important

[46] Tollens and Wigand, *Annalen*, **265**, 317 (1891).

[47] Berthelot, *Ann. Chim. Phys.*, (3), **38**, 41 (1853).

[48] Böeseken, *Rec. Trav. Chim. Pays-Bas*, **29**, 330 (1910).

general method for the condensation of organic compounds, which we owe to Friedel and Crafts,[49] and of which the principal applications and methods of operation will be set forth in Chapter XX.

It acts powerfully on hydrocarbons to cause decompositions as well as molecular condensations (Chapter XXI).

88. Ferric Chloride. Anhydrous ferric chloride can be substituted for aluminum chloride in many of its catalytic reactions. It gives good results as agent of direct chlorination or bromination (285) and even of iodination (295).

It can serve as catalyst in the production of acetals (781 and 783).

It can replace aluminum chloride in the Friedel and Crafts synthesis (899) as well as in analogous condensations (902).

89. Zinc Chloride. This chloride, having a strong affinity for water, is frequently employed as a dehydrating agent. The reactions which it produces are frequently considered as not catalytic, but a closer examination classes them as such, since they are generally produced by small amounts of the salt, smaller than would be required for a chemical reaction.

Thus zinc chloride is a well defined catalyst in the acetylation of glycerine by acetanhydride (761), in the crotonization of aldehydes (795), and in the formation of substituted indols by the decomposition of phenylhydrazones (633). Its rôle is less easy to define and to distinguish from that of an ordinary chemical reagent in quite a number of reactions, such as the condensation of benzaldehyde with nitromethane,[50] with chloral hydrate,[51] with ethyl orthoformate,[52] or with phthalic anhydride,[53] or of phenols or polyphenols with aromatic amines,[54] or with fatty acids.[55]

Anhydrous zinc chloride can replace aluminum chloride in the Friedel and Crafts synthesis (899), and can also produce polymerizations (211).

Chlorides of Cobalt, Nickel, Cadmium, and Lead. These decompose alkyl chlorides after the manner of barium chloride (876).

90. Stannic Chloride. In certain condensations of organic molecules as of aliphatic aldehydes with phenols,[56] its rôle as a catalyst is difficult to define, as has been said of zinc chloride, or in the

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[49] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), 1, 489 (1884).

[50] PRIEBS, *Annalen,* 225, 321 (1884).

[51] BOESSNECK, *Berichte,* 19, 367 (1886).

[52] FISCHER and KÖRNER, *Berichte,* 17, 98 (1884).

[53] FISCHER, *Annalen,* 206, 86 (1881).

[54] CALM, *Berichte,* 16, 2786 (1883).

[55] GOLDZWEIG and KAISER, *J. prakt. Chem.,* (2), 43, 91 (1891).

[56] FABINYI, *Berichte,* 11, 283 (1878).

formation of phthaleïnes from phenols and phthalic anhydride,[57] but it is well established in the addition of acid chlorides to ethylene hydrocarbons (241).

Chlorides of Antimony, Molybdenum, Thallium and Uranium. These can be used as chlorination catalysts (286).

91. Cuprous Chloride, Bromide, and Iodide. These cause the decomposition of diazonium salts with the hydracids into the corresponding aromatic halogen compounds, with the elimination of nitrogen (the Sandmeyer reaction) (606). They can bring about the decomposition of phenylhydrazine (611) as well as the production of indols by the decomposition of the phenylhydrazones (633). Cuprous chloride causes the scission of chlorinated hydrocarbons (879). Cuprous iodide has been employed with success in the phenylation of primary aromatic amines (901).

92. Mercuric Chloride. This accelerates the isomerization of isobutyl bromide (200) and permits acetaldehyde to be prepared by the hydration of acetylene (309).

93. Aluminum Bromide. This is advantageously employed as catalyst in bromination. It causes rapid transformation of propyl bromide into the isomeric isopropyl bromide (199).

94. Potassium Iodide. Organic chlorine derivatives usually react with less facility than the corresponding iodides. Their action can be greatly facilitated by the addition of 10% potassium iodide, which apparently permits the progressive transformation of the chloride into the more reactive iodide.[58]

95. Potassium Cyanide. It acts as an efficient catalyst of aldolization (220) and even of polymerization in the strict sense (230).

The *double cyanide of potassium and copper* has been employed as oxidation catalyst (268).

INORGANIC SALTS OF OXYGEN ACIDS

96. A large number of these salts can act as catalysts in organic reactions.

Salts formed from weak acids or from weak bases or ammonia, readily separated by dissociation, usually show effects which could be produced by their constituents separately.

97. Alkaline Carbonates. These may be used advantageously in place of caustic potash in reactions of aldolization or of analogous condensations (219 and 236).

[57] BAEYER, *Annalen,* **202,** 154 (1880).
[58] WOHL, *Berichte,* **39,** 1951 (1906).

Potassium Bisulphate. This salt can act as free sulphuric acid, either in esterification or in the direct production of acetals, or in condensations effected with elimination of water such as that of dimethyl aniline with benzaldehyde.[59]

Ammonium Sulphate, Nitrate, and Chloride. These can act as the free acids in esterification, or in analogous reactions, such as the production of acetals (783).

98. Barium and Calcium Carbonates. These are equivalent to the free oxides.

Calcium Sulphate. Either as the hydrate, or dehydrated below 400°, it possesses a certain activity for dehydrating alcohols into the ethylene hydrocarbons (718).

99. Aluminum Sulphate and Phosphate. These are dehydration catalysts analogous to free alumina (718).

Silicates. Clay and *kaolin,* hydrated silicates of aluminum, catalyze the dehydration of alcohols as does alumina (717).

Broken glass, which is a mixed silicate of variable composition, has properties which vary with this composition. In the decomposition of formic acid around 300°, Jena glass yields mainly carbon dioxide and hydrogen, while the ordinary white glass gives water and carbon monoxide, approaching pure silica (828).

Pumice, in spite of its porous structure, is only slightly active as a catalyst and approaches silica in its action.

100. Ferrous and Manganous Salts. In the presence of water, these are active oxidation catalysts (264). Thus the presence of various manganous salts aids the oxidation of oxalic acid solutions.[60]

101. Magnesium Sulphate. This is an excellent catalyst for the dehydration of glycerine into acroleïn (725).

102. Mercuric Sulphate. This can cause the hydration of acetylene hydrocarbons into ketones (309), and the oxidation of organic compounds by fuming sulphuric acids (272). Its presence determines the nature of the isomers produced in the direct sulphonation of aromatic molecules (816). It can also determine isomerizations (195).

103. Copper Sulphate. In Deacon's process, it is copper sulphate that catalyzes the oxidation of hydrochloric acid by air at 430° with the production of chlorine. It can, although with disadvantage, replace mercuric sulphate in the oxidation of organic compounds by fuming sulphuric acid (272).

[59] WALLACH and WÜSTEN, *Berichte*, 16, 149 (1883).
[60] JORISSEN and REICHER, *Zeit. physik. Chem.*, 31, 142 (1900).

VARIOUS COMPOUNDS

104. Ammonia. The presence of ammonia favors the polymerization of cyanamide (233).

Amines. Aliphatic primary and secondary amines are of use as catalysts in the complex reactions in the vulcanization of rubber. *Piperidine* has been suggested for the purpose.[61] Nitrosodimethylaniline has been recommended in the ratio of 0.3 to 0.5 part to 100 parts caoutchouc and 10 parts sulphur at 140°.[62]

Alkyl Halides and Esters. A small quantity of an alkyl iodide, especially *methyl* or *ethyl iodide,* greatly facilitates the preparation of the organo-magnesium compounds in the Grignard reaction, particularly when chlorides are used (302).

Acetaldehyde, heated to 100° with *ethyl iodide,* condenses to paraldehyde.[63]

Ethyl oxalate, by its presence, favors the reduction of ethylene bromide to ethyl bromide by the alloy of sodium and zinc.[64]

Ethyl nitrite, in alcohol solution, causes the transformation of thiourea into ammonium isosulphocyanate.

Ethers. Ethyl ether, as well as amyl ether, and anisol, $C_6H_5.O.CH_3$, plays an important rôle as catalyst in the formation of the organo-magnesium complexes in the Grignard reaction (300).

105. Aldehydes. Acetaldehyde provokes the hydration of cyanogen to oxamide (311).

106. Organic Acids. *Acetic acid* can sometimes act, after the fashion of mineral acids, to cause combinations with elimination of water, as in the production of acetals (780). Its catalytic rôle can be disputed in the condensation of benzaldehyde with malonic acid.[65]

Isoprene heated with acetic acid is transformed into artificial rubber (215).

Oxalic acid acts like hydrochloric or phosphoric acid in the polymerization of aldehydes.

107. Alkaline Acetates. Sodium acetate is a quite active dehydration catalyst. It produces the crotonization of aldehydes (795) as well as their simple polymerization. It is employed as a catalyst to aid in the esterification of alcohols by acetanhydride.

Quite a large number of organic condensations, which take place

[61] BAYER & Co., *German Patent,* 265,221 (1912), *C.* 1913, (2), 1444.
[62] PEACHEY, *English Patent,* 4,263 of 1914.
[63] LIEBEN, *Annalen, Suppl.,* **i,** 114 (1861).
[64] MICHAEL, *Am. Chem. J.,* **25,** 419 (1901).
[65] CLAISEN and CRISMER, *Annalen,* **218,** 155 (1883).

with elimination of water, have as their basis the use of sodium acetate, but it is usually employed in such large proportions that its catalytic rôle is masked. This is the case in the condensation of phthalid with phthalic anhydride to form diphthalid.[66]

Likewise *potassium acetate* permits the condensation of acetic acid with phthalic anhydride to form phthalylacetic acid.[67]

It is under the same conditions — that is, employed in large quantity — that sodium acetate causes acetanhydride to act on benzaldehyde to form cinnamic acid in Perkin's synthesis.[68]

108. Nitroso Compounds. The *nitroso* derivatives of *methylaniline, dimethylaniline,* and *diphenylamine* are accelerators in the vulcanization of caoutchouc. The same property belongs to *nitrosophenol* and *nitrosonaphthol* but not to the isomeric nitrosoamines.[69]

109. Alkyl Cyanides. *Methyl* and *ethyl cyanides* are active catalysts in the reaction of sodium with alkyl iodides, or with similar compounds (605).

110. Fibrine. It may be recalled that *fibrine* catalytically decomposes hydrogen peroxide very rapidly.

DURATION OF THE ACTION OF CATALYSTS

111. It would seem, by definition, that the action of catalysts should be prolonged indefinitely, and this perpetuity would be assured to them if they did not suffer any alteration in the course of the reactions which they effect. If any change does take place, as is most frequently the case with solid catalysts acting in gaseous or liquid media, an alteration of the surface, even slight, brings on progressive diminution of activity which may go as far as total suppression.

In hydrogenations carried on by nickel in gaseous systems, using pure and sufficiently volatile substances and thoroughly purified hydrogen, at a carefully regulated temperature, the action can be continued by the same metal a very long time without appreciable weakening. Sabatier and Senderens were able to effect the transformation of benzene into cyclohexane for more than a month with the same nickel, the operation being interrupted every evening and resumed in the morning. The slight oxidation which the metal suffered over night, in the cold tube, caused no inconvenience because the oxide was again reduced by the hydrogen at the beginning of the next run.[70]

[66] GRAEBE and GUYE, *Annalen,* **233,** 241 (1886).

[67] GABRIEL and NEUMANN, *Berichte,* **26,** 925 (1893).

[68] PERKIN, *J. Chem. Soc.,* **31,** 388 (1877).

[69] PEACHEY, *J. Soc. Chem. Ind.,* **36,** 424 (1917).

[70] SABATIER and SENDERENS, *Ann. Chim. Phys.,* (8), **4,** 334 (1905).

112. **Poisoning of Catalysts.** On the contrary, traces of chlorine, bromine, iodine and sulphur in the system are frequently sufficient to suppress the activity of the nickel entirely. It appears to be *poisoned*. Benzene which is not absolutely free from thiophene can not be hydrogenated. An infinitely small amount of bromine in phenol renders it incapable of being changed into cyclohexanol.[71] Chlorine or bromine derivatives of benzene have never been hydrogenated since the first portions of these compounds alter the metal immediately in an irremediable manner.

113. But the conditions under which this poisoning of the metal take place are quite complex. The presence of free halogens or halogen acids in the hydrogen is much less harmful than the presence of combined halogen in the vapors submitted to hydrogenation. This has been observed by Sabatier and Espil in the hydrogenation of benzene.[72]

In an apparatus in which the hydrogenation of benzene was progressing regularly over nickel at 180°, the benzene was replaced by benzene containing 0.5% iodine. The hydrogenation continued for several hours with an excellent yield. The escaping hydrogen, after the condensation of the cyclohexane, disengaged abundant fumes of hydriodic acid showing that the iodine had been hydrogenated by the catalyst. The operation was interrupted after 130 g. of cyclohexane had been collected and it was found that the nickel had combined with iodine in the first half only of the tube. This half was incapable of carrying on the hydrogenation but the other half was unhurt. The poisoning of the metal by the iodine had taken place only slowly and step by step; the hydriodic acid had had, on its own account, no harmful effect and had not converted into the iodide the metal the surface of which was covered with an unstable hydride which produced the hydrogenation (167). Doubtless the fixation of the hydrogen on the iodine and the benzene in contact with the nickel is much more rapid than the reaction of the nickel with the iodine or with the hydriodic acid. As in the direct hydrogenation of unsaturated hydrocarbons (422), the metal protects itself, by its own action, against the permanent alteration which would render it inactive.

114. Similar results have been obtained, by the same authors, in hydrogenating benzene with hydrogen containing hydrogen chloride, but if traces of brombenzene or chlorbenzene are added to the benzene, the production of cyclohexane ceases almost immediately and the nickel is incapable of regaining its activity.

[71] SABATIER and MAILHE, *Compt. rend.*, **153**, 160 (1911).
[72] SABATIER and ESPIL, *Bull. Soc. Chim.*, (4), **15**, 778 (1914).

It is plain that free chlorine or bromine in the hydrogen, unlike iodine, would produce a definite poisoning of the metal since they would offer the possibility of direct substitution in the benzene which iodine does not do.

Sabatier and Espil have likewise been able, for several hours, to transform into cyclohexane benzene containing 10% of carbon disulphide, but traces of thiophene added to the benzene stopped the reaction at once.

115. The use in the oil industry (937 et seq.) of nickel as hydrogenation catalyst suspended in the liquid, has led to the determination of the greater or less toxicity of a number of substances which may be present in small amounts in the oils to be treated.

The soaps formed from the various metals or oxides are, from this point of view, very dissimilar: while those of nickel, thorium, cerium, aluminum, and calcium are absolutely without harmful effect, those of potassium, barium, zinc, cadmium, lead, and uranium are harmful.

The nickel salts of organic monobasic acids, as well as of lactic, oxalic, and succinic acids, are without effect. The same can be said of the free fatty acids such as acetic and stearic, but oxystearic, malic, tartaric and citric acids are true poisons for the nickel catalyst. Toxicity is also shown by calcium hydroxide, potash, boric acid, ammonium molybdate, as well as by sulphur, selenium, red phosphorus, glycerine, lecithine, morphine, strychnine, amygdaline, and cyanides. Tin and aluminum in powder are without action, but iron, lead, and zinc are harmful.[73]

116. With a platinum catalyst, the extreme toxicity of compounds of sulphur,[74] phosphorus and arsenic and of cyanides, etc., has long been known. The activity of colloidal platinum is diminished or destroyed by a large number of materials. Their toxicity has been measured by means of the velocities of decomposition of hydrogen peroxide and it has been suggested to designate by the term *toxicity*, the dilution (in liters per gram-molecule) at which the velocity of decomposition in contact with 0.000,01 gram-atom of platinum, is reduced one-half.[75]

Among the violent poisons, *hydrocyanic acid* stands at the head with toxicity 21,000,000, followed by *iodine* with 7,000,000, *mercuric chloride* with 2,500,000, sodium hyposulphite, carbon disulphide, carbon monoxide, and phosphorus. Among the moderate poisons, are placed *aniline* with toxicity, 30,000, *bromine* with 23,000, *hydrochloric*

[73] Seiichideno, *J. Chem. Ind., Tokyo,* **21,** 898 (1918).

[74] Turner, *Pogg. Ann.,* **2,** 210 (1824).

[75] Bredig and Ikeda, *Zeit. phys. Chem.,* **37,** 1 (1901).

acid with 3,100, oxalic acid, amyl nitrite, arsenious acid, and ammonium chloride. Among the feeble poisons, are found *phosphorus* acid, 900, sodium nitrite, and hydrofluoric acid, while potassium chlorate, alcohol, ether and pinene have no toxicity and formic acid, hydrazine, and dilute nitric acid are rather favorable. These toxicity coefficients would certainly be very different if measured with platinum black or sponge.[76]

117. **Platinum black** is very sensitive to the poisons enumerated for colloidal platinum. Traces of *potassium cyanide* are sufficient to take from the metal all power to hydrogenate the aromatic nucleus, and also to weaken greatly the hydrogenation of ethylene bonds.[77]

Contrary to what has been said about colloidal platinum, the hydrogenation velocity of pinene is diminished if it is dissolved in *alcohol* or in any substance capable of furnishing alcohol *e. g.* ether or ethyl acetate. The fatty acids have little action, except *formic*, which has a marked toxic effect.[78]

118. **The Fouling of Catalysts.** Other causes of alteration can come in to bring on the decline of catalysts. It happens quite frequently that, along with the principal reaction, there are side reactions which become more important at elevated temperatures and which give rise to highly condensed substances which are only slightly volatile, carbonaceous or tarry. Such substances are slowly deposited on the active surfaces where they hinder the contact with the gas, rendering the useful reaction slow.

In hydrogenations, or decompositions by finely divided metals, the more active the metals, the more rapid are formations of this sort. The most fiery catalysts are the most rapidly enfeebled.

The decline of a catalyst, either from poisoning or fouling, is indicated by the diminishing of the yields in the reaction which it catalyzes.

When a fatigued nickel catalyst is dissolved in dilute hydrochloric acid, fetid hydrocarbons are evolved with the hydrogen and brown carbonaceous or viscous materials are deposited.

119. It can be seen that an analogous enfeeblement will take place when the reaction produces a material which is only slightly volatile at the temperature of the tube and which impregnates the metal more or less rapidly thus opposing its regular activity. This takes place in the hydrogenation of aniline in the presence of nickel at 190°, since

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[76] See comprehensive article by BANCROFT *J. Phys. Chem.*, **21**, 767 (1917).

[77] MADINAVEITIA, *Soc. Espan. Phys. Chim.*, **11**, 328 (1913).

[78] BÖESEKEN, VAN DER WEIDE and MOM, *Rev. Trav. Chim. Pays-Bas*, **35**, 260 (1916).

there is produced, in addition to the cyclohexyl amine boiling at 134°, two other amines which are only slightly volatile, dicyclohexyl amine and cyclohexyl aniline, which boiling above 250°, are carried off with difficulty by the hydrogen and remain partly in the liquid form in contact with the metal.

120. It is to avoid analogous effects that it is necessary to watch that the metal is never *wetted* by an excessive flow of the liquid which is being used or in consequence of an accidental lowering of the temperature of the tube. In the preparation of cyclohexanol or its homologs by the hydrogenation of phenol or the cresols, the reaction is carried on at a temperature only a little above the boiling points of the liquids and it happens sometimes that the nickel is wetted by the liquid. The catalyst immediately becomes nearly inactive, because the surface is, without doubt, altered permanently by contact with the liquid phenol or cresol.

121. Catalytic hydrogenation by finely divided metals is, to a certain extent, comparable to the action of the figured ferments.[79] As with these, there are three periods, an initial period in which the catalyst adapts itself to its function, a period of normal activity and a period of decline, ending in the death of the ferment.

The first period is a variable state and is usually of short duration: it corresponds, without doubt, to the superficial modification which the metal undergoes when the atmosphere of pure hydrogen which surrounded it, is replaced by a mixture of the vapors with hydrogen.

The second period, that of normal functioning, is usually very long and would be indefinite unless something is passed in or is produced which can alter the surface of the metal. Such substances may enter with the hydrogen or with the substance to be hydrogenated or may be produced in the reaction.

122. Catalytic oxides, although less sensitive than the metals to chemical alterations of their surfaces, may, nevertheless, suffer from this cause notable diminution of activity even to complete suppression of their function. In many cases they are so fouled that they are weakened or paralyzed.

123. **Regeneration of altered Catalysts.** In so far as the alteration of metallic catalysts is due simply to fouling by deposits of carbon or of tarry substances, calcination in a current of air is suf-

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[79] "Figured ferments" is an obsolete expression for "organized ferments," meaning ferments in which cells can be found with the microscope, as in the yeasts; in contradistinction to such ferments as saliva, etc. The cells were spoken of as "figures," hence "figured ferments."—H. S. JENNINGS.

ficient to burn off these substances, converting the metal (nickel, iron, copper) into the oxide which a new reduction, carried out at a suitable temperature, will reconvert to the metal. These operations can be carried out in turn in the tube itself in which the catalysis takes place.

This procedure is not suitable for platinum black, which by being heated to redness loses nearly all of its catalytic activity (63).

It does not serve well for the greater part of the metal oxides which are greatly diminished in activity by heating to a high temperature; but it does serve well for *thoria* which has been fouled by long use (708).

124. Metallic catalysts poisoned by vapors of chlorine, bromine, iodine, sulphur, etc., are difficult to revivify except by dissolving in a suitable acid and working over completely.

Calcination does not remove chlorine from slightly chlorinated nickel. The action of hydrogen reduces the chloride to the metallic state below 400°, but the resulting metal is in a peculiar fibrous state and is incapable of reducing benzene to cyclohexane. Even after oxidation and a second reduction it is a poor catalyst.

125. It can be slowly restored to complete activity by employing it for some time in the reduction of nitrobenzene to aniline, work which poisoned nickel is still capable of doing. The aniline which is produced contains increasing amounts of cyclohexyl amine. After some hours of this treatment the power of the metal to produce cyclohexane from benzene is completely restored. On the contrary, poisoning by bromine or iodine seems to resist this treatment.[80]

MIXTURE OF CATALYSTS WITH INERT MATERIALS

126. The desire to increase the active surface of solid catalysts had led to disseminating them over inert porous materials such as pumice, asbestos, infusorial earth, and various metal salts. This practice has appeared specially advantageous for expensive catalysts such as platinum and palladium. Thus in the manufacture of sulphuric acid by the contact process, the catalytic masses are either *platinized asbestos,* or anhydrous *magnesium sulphate* impregnated with platinum (about 14 g. metal per kilogram of sulphate).

Nickeled pumice which has been employed by certain chemists in place of nickel powder for hydrogenations, is readily prepared by incorporating the crushed pumice in a thick paste of precipitated

[80] SABATIER and ESPIL, *Bull. Soc. Chim.,* (4), **15,** 779 (1914).

nickel hydroxide, drying in the oven, and finally reducing in the tube that is to be used for the hydrogenations.[81]

127. In the case of catalytic metals which have to be carried to a red heat (932), the use of inert siliceous carriers may have serious consequences owing to the formation of silicates which may suppress the activity of the metal. In such cases it is best to use carriers free from silica, such as magnesia, alumina, natural bauxite, lime or carbonate of calcium, etc., either by employing these substances in powders intimately mixed with the oxides, the reduction of which is to furnish the metals, or by previously sticking together these mixtures in little lumps with the aid of non-siliceous materials (Sabatier and Mailhe).

128. In certain cases the use of inert supports for solid catalysts can lead to serious trouble. When the catalyst is to be heated on a furnace, it is disposed in a thin layer in the tube. By a fear entirely unjustified, in view of the great velocity of diffusion of hot gases, some have doubted the sufficiency of the contact between the gas, circulating too freely in the upper part of the tube, and the catalyst. Guided by this thought, the whole height of the tube has been filled with the pumice impregnated with the catalyst. But these conditions are not favorable, since the temperature varies much from bottom to top of the tube. On the contrary, filling the tube entirely with the catalytic mass presents no inconvenience when the tube is heated all around as, for example, by an electric resistance wound around it.

[81] BRUNEL, *Ann. Chim. Phys.*, (8), **6**, 205 (1905).

CHAPTER III

THE MECHANISM OF CATALYSIS

129. The extreme diversity of catalytic reactions makes it evident that difficulties will be encountered in giving an explanation that will fit all cases.

Berzelius, who was the first to define catalytic phenomena and to give them this name (4) did not really furnish any explanation for them and found only vague terms with which to characterize the *catalytic force* which he regarded as the cause of reactions of this kind. " It is evident," said he, " that the catalytic force acts principally by means of the polarity of the atoms which it augments, diminishes or changes. In other words, the catalytic force manifests itself by the excitation of electrical relations which, up to the present, have escaped our investigation." [1] And he adds: " From all that precedes, it follows necessarily that the *sources of power* (light, heat, electricity) contain the cause of the activity of matter, which, without their influence, would be inert and in a state of unalterable and eternal repose."

To the mind of Berzelius, catalytic forces are then of the order of the sources of power " different effects of one first cause which, under definite circumstances, pass from one modification into another." [2] But their nature remains no less mysterious: the calorific phenomena, sometimes intense, which frequently accompany catalyses, may be the consequences rather than the determining cause.

130. In a great number of catalyses, such as are realized by platinum black and by finely divided metals prepared by reduction of oxides, the porous state seems, at least at first sight, to be the determining cause of the catalytic activity and this thought is the basis of the explanation that has been given of the mechanism of catalysis and which, accepted readily by many chemists, has been usually elaborated in treatises.

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[1] BERZELIUS, *Traité de Chemie*, 2nd Ed., Paris, 1845, I, 112.
[2] BERZELIUS, *loc. cit.*, 36.

PHYSICAL THEORY OF CATALYSIS

131. Porous materials, whose surfaces are very large as compared with their masses, enjoy the property of absorbing gases with more or less energy. A case of the absorption of gases by solids, that has been much studied, is that of wood charcoal.

When 1.57 g. coconut charcoal, corresponding to 1 cc. of compact carbon, has been heated to redness and cooled under mercury, it absorbs in the cold (at 15° and 760 mm.) quite various volumes of gases, all the way from 2 cc. for argon to 178 cc. for ammonia. These volumes increase nearly proportionally with pressure and decrease greatly when the temperature is raised.

The volume mentioned above for ammonia shows that this gas, if compressed to a volume equal to the total volume of the charcoal would require a pressure of 178 atmospheres, and as this gas is liquefied at 15° under 5.5 atmospheres, it is necessary to assume that the ammonia exists in the pores of the charcoal in the liquid condition, in which it would occupy a volume of about 0.2 cc. (from the known density of liquid ammonia).

The absorption of the gas by the carbon liberates much heat and this amount of heat is even larger than that obtained by the liquefaction of the gas. Thus the amounts of heat per cubic centimeter of gas are: [3]

	Absorption by *carbon*	*Liquefaction*
Sulphur dioxide	0.61 to 0.47 cal.	0.26 cal.
Ammonia	0.45 to 0.33 cal.	0.20 cal.

For ammonia, the heat of absorption is little different from the heat of solution in water and is much larger than the heat of solution in the case of sulphur dioxide.[4]

For hydrogen, the heat of absorption by carbon is six times the heat of liquefaction (Dewar).

132. To explain these singular phenomena, it is assumed that the enormous attraction of the surface of the cavities of the wood charcoal causes the accumulation of the gases in the cavities, at pressures which are not very great for the permanent gases (argon, hydrogen, nitrogen), however, exceeding 35 atmospheres for oxygen, but which are very high for the easily liquefiable gases, generally much greater

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[3] FAVRE and SILBERMANN, *Ann. Chim. Phys.*, (3), **37**, 465 (1853). REGNAULT, *Ibid.*, (4), **24**, 247 (1871).

[4] LE CHATELIER, *Leçons sur le Carbone, Paris*, 1908, p. 133.

than the pressures required for liquefaction: this liquefaction would be actually accompanied by a strong compression of the thin layer of liquid produced on the carbon walls. This compression would be responsible for the excess of the heat of absorption over that of liquefaction.

133. An analogous evolution of heat has been observed when any liquid whatever is absorbed by a solid having a very large surface, such as a fine powder, and is called heat of *imbibition*.

Powdered *quartz*, with grains averaging 0.005 mm. diameter, disengages per gram, when wetted:

With water .... 14 calories
With benzene .... 4 "

Calculating the surface of the grains, the heat of wetting by water appears to be 0.00105 cal. for 1 sq. cm. of quartz at 7°.

It has been shown likewise, that the wetting by water of 1 g. starch evolves 22 calories, 1 g. wood charcoal, 7 calories, 1 g. alumina, 2 calories.

134. The absorption of gases in the pores of the carbon is equivalent to compressing the gases to a greater or less pressure. Simultaneously there is the liberation of considerable heat by the absorption. It is imagined that the heat and pressure cause reactions to take place. Hydrogen and chlorine may unite in the cold when they meet each other thus in the pores of the carbon, and it is the same way with carbon monoxide and chlorine and with hydrogen sulphide and oxygen.

The oxygen which is absorbed combines little by little with the carbon in the cold to give carbon dioxide. When the gases are pumped out of wood charcoal, which has been exposed to air, scarcely anything is obtained except nitrogen and carbon dioxide.

It would seem then that porous carbon should be a universal catalyst for all gas reactions, lowering the reaction temperatures greatly. However, except for the formation of *carbonyl chloride* (282), carbon is a mediocre catalyst and of little use, doubtless because gaseous interchanges do not take place rapidly enough in it.

135. Various powdered substances have greater or less power of absorbing gases, but generally, especially for oxides and salts, this power is not great.

Finely divided metals are, in certain cases, able to absorb considerable amounts of gases, but this aptitude is always specific and limited to a small number of gases. In the case of charcoal, the amounts of various gases absorbed are roughly in proportion to their

ease of liquefaction, while with metals the absorption is markedly characterized by a sort of selective affinity.

136. It is one of the most difficultly liquefiable gases, *hydrogen*, that is absorbed the most readily by metallic powders. The maximum of such absorption is shown by *palladium*, which, in the form of sponge, can absorb 680 to 850 times its own volume of hydrogen, whatever be the pressure of the gas, provided the pressure be not too low: for all of the hydrogen is given up in a vacuum, even in the cold.[5]

At 20°, *platinum black* absorbs 110 volumes of hydrogen, whatever the pressure, provided it is more than 200 mm., and here, likewise, the hydrogen is given up in a vacuum.[6]

Reduced cobalt can absorb 153 volumes of hydrogen, finely divided *gold*, 46, reduced *iron* or reduced *nickel*, up to 19, and reduced *copper*, only 4.[7]

137. The precious metals have an analogous, though less energetic affinity for oxygen. Thus *platinum black* absorbs up to 100 volumes of oxygen in the cold and here again this amount is not increased by additional pressure and all of the gas is given up in a vacuum.

Finely divided gold and silver can also take up greater or less amounts of oxygen.[8]

138. The activity of these finely divided metals, as hydrogenation or oxidation catalysts, would then be due to their power to absorb hydrogen or oxygen along with the vapor which is to be transformed. The compression and local heating thus produced would cause the reaction to take place which without this help would have required a much higher temperature, frequently a temperature so high that the products would not be stable.

The dehydrations of alcohols which are effected by contact with alumina, would result from the condensation of the alcohol vapors in the pores of the alumina, this condensation producing effects comparable to superheating the vapors.

139. The powdered or porous state would be a sufficient condition to produce such effects, since a body containing an infinite number of very small cavities, offers the possibility of realizing simultaneously

    [5] Mond, Ramsay, and Shields, *Phil. Trans. Roy. Soc.*, 186, 657 (1896). *Proc. Roy. Soc.*, 62, 50 and 290 (1897). Dewar, *Chem. News*, 76, 274 (1897).

    [6] Mond, Ramsay and Shields, *Phil. Trans. Roy. Soc.*, 186, 675 (1896).

    [7] Moissan, *Traité de Chimie Mineral*, I, 13.

    [8] Neumann, *Monatsh.*, 13, 40 (1892). Mond, Ramsay and Shields, *Proc. Roy. Soc.*, 62, 50 (1897) and *Zeit. phys. Chem.*, 25, 657 (1898). Ramsay and Shields, *Phil. Trans. Roy. Soc.*, 186, 657 (1896). Engler and Wöchler, *Zeit. anorg. Chem.*, 29, 1 (1901).

all possible temperatures and all possible pressures thus causing a great number of reactions by condensation and heating.[9] To this local pressure, there is added also, in the case of metals, the effect of immediate contact with a good conductor and, consequently, electrical influences which might aid.[10]

140. A reaction which, without the aid of the catalyst, would take place at an infinitely slow rate, at the temperature of the experiment, would thus receive, on account of the pressure of the catalyst, an immense acceleration and go to completion in a relatively short time.

Catalysis would then be, as Ostwald[11] has defined it, only the acceleration of a chemical phenomenon which otherwise would take place slowly. The presence of the catalyst in the system suppresses the chemical friction which slows up the reaction to the point of stopping it entirely. Its rôle would then be similar to that of oil in clockwork, the movement of which it accelerates, though the forces which produce the movement are not increased.

141. This physical explanation, applicable to all porous catalysts, meets with objections numerous and difficult to get rid of.

Right at the start, the cause which determines the condensation of gases and vapors in the pores of a solid remains mysterious and inexplicable; this physical attraction of solids for gaseous substances presents no visible relation to the properties of the gases. The absorption by wood charcoal is indeed greater for gases which are readily liquefied, but it is just the other way with platinum and various metal powders where the gas that is most absorbed is hydrogen which is very difficult to liquefy.

The same theory is difficult to apply to the case where hydrogen is taken up with the aid of platinum black or nickel held in suspension in a liquid medium (Chapters XI and XII), and even more difficult where the catalyst is *colloidal platinum* or *palladium:* for it is difficult to see how high local pressures and temperatures could be developed in such cases.

142. Furthermore, a purely physical conception of the causes of the reaction does not take account of the *specificity* of *catalysts* and of the remarkable diversity of the effects produced.

At the same temperature, 300°, the vapors of an alcohol, *isobutyl,* for example, decompose:

in the presence of *copper*, into aldehyde and hydrogen, exclusively;
in the presence of *alumina,* into isobutylene and water, exclusively;

[9] Duclaux, *Compt. rend.,* **152**, 1176 (1911).
[10] van't Hoff, *Leçons de Chim. Phys.,* 1898, 3, 216.
[11] Ostwald, *Rev. Sci.,* **1902** (1), 640.

in the presence of *uranium oxide,* both ways, giving at the same time the aldehyde and isobutylene.

Manganous oxide gives the same decomposition as copper, only slowly.

If we assume that the metallic characteristic of conductivity accounts for the fundamental difference between copper and alumina; we can not explain the differences between alumina, and the oxides of manganese and uranium, if the physical condensation in the pores of the catalyst is the sole cause of catalysis.

The action of the catalytic oxide can not be entirely like an elevation of temperature, since the direction of the reaction is intimately connected, not with the physical state of the oxide, but with its chemical nature.

143. The decomposition of formic acid furnishes a no less striking example of the specificity of catalysts (821). Finely divided metals and likewise *zinc oxide,* decompose this acid into hydrogen and carbon dioxide exclusively, but at the same temperature, *titanium oxide* gives carbon monoxide and water exclusively, while certain oxides, as *thoria,* bring about a mixed reaction, more or less complicated by the production of formaldehyde and even of methyl alcohol.

Yet from the physical point of view there does not appear to be any great difference between the oxides of zinc, titanium, and thorium.

144. Furthermore, this explanation of catalysis can not possibly apply to the effects of liquid catalysts in homogeneous systems and it is hard to imagine that there are fundamental differences between the various kinds of catalysis.

CHEMICAL THEORY OF CATALYSIS

145. An entirely general explanation of catalytic phenomena can be based on the idea of the temporary formation of unstable chemical compounds which, serving as intermediate steps in the reaction, determine its direction or increase its velocity.

In order to arrive at a clearer idea of the catalytic mechanism, a special case can be first considered which can be classed as catalytic and which can be designated by the name *reciprocal catalysis.*

146. **Reciprocal Catalysis.** Suppose two distinct chemical systems capable of reacting independently, each on its own account: however, each one of them, if left to itself, remains in false equilibrium or, at least, reacts with extreme slowness. But if these two systems

are mixed, they mutually catalyze each other and the two reactions proceed simultaneously very rapidly in correlative proportions.[12]

147. An example is furnished by hydrogen peroxide, opposed by *chromic acid*, H_2CrO_4. The hydrogen peroxide tends to decompose into water and oxygen, but in the cold, this spontaneous decomposition is very slow and would require more than a year.

The chromic acid solution, acidified with sulphuric acid, is also stable in the cold, but, if heated it decomposes with evolution of oxygen. On heating, we would have:

$$3 \ H_2O_2 = 3H_2O + 3 \ O$$

and $$2 \ H_2CrO_4 + 3 \ H_2SO_4 = Cr_2(SO_4)_3 + 5 \ H_2O + 3 \ O.$$
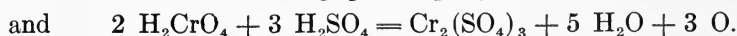
But if the two solutions are mixed cold, in the exact proportions represented by the formulae above, there is immediate decomposition, simultaneous and complete, of both the hydrogen peroxide and the chromic acid, and this decomposition, manifested by a brisk effervescence of oxygen, takes place in such a manner that the amount of oxygen coming from the hydrogen peroxide is exactly the same as that from the chromic acid.

This proportionality indicates the cause of the reaction, which is apparently the production of an unstable combination of hydrogen peroxide and chromic acid in the proportion $3 \ H_2O_2 : 2 \ H_2CrO_4$. As soon as this compound is formed, it decomposes, with liberation of oxygen, leaving water and chromic oxide which dissolves in the sulphuric acid present.

This fugitive combination, the temporary formation of which destroys the false equilibrum of the two systems, really exists: for it appears as an intense blue coloration, when the two liquids are mixed, and can even be isolated. If a dilute solution of hydrogen peroxide is poured into a slight excess of chromic acid: in place of a stormy effervescence a blue solution is obtained. When this is shaken with ether, the dark blue unstable compound passes into the ether. The evaporation of the ether at —20°, leaves a dark blue oil, which, on warming to room temperature, decomposes into chromic oxide, water, and oxygen. We have in succession,[13]

$$2H_2CrO_4 + 3 \ H_2O_2 = 4 \ H_2O + H_2Cr_2O_{10}$$
$$H_2Cr_2O_{10} = Cr_2O_3 + H_2O + 3 \ O_2.$$
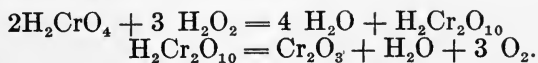
148. Another example of reciprocal catalysis is offered by an acid solution of potassium permanganate opposed by hydrogen peroxide.

[12] SABATIER, *Rev. gén. de Chimie pure et app.*, 17, 185 (1914).
[13] MOISSAN, *Traité de Chimie Min.*, I, 275 (1904).

The permanganate which is itself an energetic oxidising agent, reduces the hydrogen peroxide immediately, and is itself reduced.   Here again there is exact equality between the amounts of oxygen coming from the two reacting substances.

A solution of potassium permanganate, acidified with sulphuric acid, is stable in the cold, but when heated there is a slow reaction:

$$2 \ KMnO_4 + 3 \ H_2SO_4 = 2 \ MnSO_4 + K_2SO_4 + 3 \ H_2O + 5 \ O.$$

Likewise the hydrogen peroxide alone would give very slowly in the cold:

$$5 \ H_2O_2 = 5 \ H_2O + 5 \ O.$$
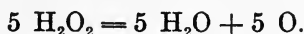
On mixing the two solutions there is immediately a vigorous effervescence, liberating 10 O.   The reaction is quantitative and is used practically for the estimation of hydrogen peroxide by titrating with standard potassium permanganate solution.   As in the case of chromic acid, this proportionality indicates the formation of an unstable compound, the decomposition of which disengages 5 O_2; but in this case it is difficult to detect.   According to Berthelot, the permanganate acts on hydrogen peroxide to substitute hydroxyl groups for the hydrogen atoms, furnishing a sort of *hydrogen tetroxide:*

$$O—OH$$
$$O—OH$$

which is very unstable and soon decomposes into water and 3 O. When the solutions are mixed at —12°, the permanganate is decolorized without the evolution of oxygen, but the colorless tetroxide, stable at —12°, decomposes on warming, liberating the oxygen. Potassium and caesium tetroxide, which are known, are the alkaline salts of this hydrogen tetroxide.[14]

Thus in reciprocal catalysis the simultaneous and correlated reactions of two systems, which apart only tend to react, are determined by the production of an unstable combination which serves as a common intermediate product for the two reactions.   This intermediate compound is sometimes visible as in the case of the *hydrogen peroxide-chromic acid* and sometimes difficult to perceive as in the case of the hydrogen peroxide-permanganate mixture.

149. Induced Catalysis.   Suppose a chemical system which tends to react but which remains in false equilibrum or undergoes change infinitely slowly.   But if another system which is reacting rapidly in an analogous manner be associated with the first, the first system is drawn into the reaction, without the second seeming to take any

[14] BERTHELOT, *Ann. Chim. Phys.* (5), **21**, 176 (1880) and (7), **22**, 433 (1901).

part in the reaction of the first, except, so to speak, setting it an example. This may be called *induced catalysis,* and, as in the case of reciprocal catalysis, there is found to be a proportionality between the two reactions.

Frequent examples of reactions of this sort are found among oxidations by oxygen gas and are called *auto-oxidations.*

150. Auto-oxidations. A large number of substances directly oxidisable by oxygen, or by air, stimulate by their own oxidation that of substances which, without this circumstance, would not be directly oxidisable.

Thus palladium hydride when allowed to oxidise spontaneously in water solution, causes intense oxidations; indigo is decolorized and potassium iodide is oxidised into potassium hydroxide and iodine; ammonia goes into nitric acid, benzene into phenol, and toluene into benzoic acid. Carbon monoxide is oxidised to the dioxide, an oxidation which ozone and hydrogen peroxide are incapable of accomplishing.[15]

Ethyl alcohol, exposed to the simultaneous action of sunlight and air, is not appreciably changed, but in the presence of xylene, which is oxidised, the alcohol goes into acetic acid: under the same conditions, amyl alcohol gives valeric acid, and mannite yields mannose.[16]

Oxidations of the same nature accompany the spontaneous oxidation of phosphorus in moist air, of turpentine, of aqueous solutions of pyrogallol, of alkaline sulphites, of ferrous hydroxide, of ammoniacal cuprous salts, of benzaldehyde, etc. Such substances are called auto-oxidisers, and experiment has shown that in every case they render *active,* that is to say, able to oxidise substances otherwise not attacked, exactly the same amount of oxygen as they use up in their own oxidation.[17]

151. The cause of the phenomenon appears to be that the auto-oxidiser takes up oxygen to form a sort of peroxide which is then destroyed in the oxidation of the associated substance.

The auto-oxidiser, A, alone would give:

$$A + \underset{\text{oxygen}}{O\text{—}O} = A\!\!<^{O}_{O} \; .$$

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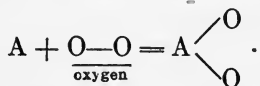
[15] Hoppe-Seyler, *Berichte,* **12**, 1551 (1879); **16**, 1917 (1883); **20**, R795 (1887); Baumann, *Ibid.,* **16**, 2146 (1883); **17**, 283 (1884). Remsen and Keiser, *Am. Chem. Jour.,* **4**, 154 (1883); **5**, 424 (1884). Leeds, *Chem. News,* **48**, 25 (1883).

[16] Ciamician and Silber, *Berichte,* **46**, 3894 (1912).

[17] Engler and Wild, *Berichte,* **30**, 1669 (1897). Engler, *Rev. gén de Chim. pure et app.,* **6**, 288 (1903).

Then in contact with the oxidisable substance, B:

$$A\underset{\underset{\text{unstable}}{\diagdown O}}{\overset{\diagup O}{\cdot}} + B = \underset{\text{stable}}{A{:}O} + \underset{\text{stable}}{B{:}O}.$$
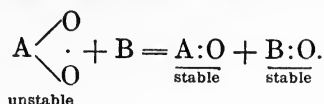
The temporary formation of the combination, $A\overset{\diagup O}{\underset{\diagdown O}{\cdot}}$, is the deter-

mining cause in the oxidation of the substance B, which would not otherwise have taken place.

In the absence of B, the second reaction would have taken place with the aid of a second molecule of A, thus:

$$A\overset{\diagup O}{\underset{\diagdown O}{\cdot}} + A = 2\,(A{:}O).$$
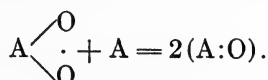
Whenever this latter reaction is sufficiently slow, the unstable peroxide can be prepared, by the action of oxygen on the auto-oxidiser alone, and may be kept for a time. Thus turpentine shaken with a large volume of air, forms a peroxide which, later on in the absence of air, can decolorize indigo, cause guaiac tincture to turn blue, or liberate iodine from potassium iodide.

The auto-oxidiser, A, is not a catalyst, since it oxidises in proportion to its own mass, and since it does not emerge unchanged from the reaction which it has caused.

152. Oxidation Catalysts. Let us suppose that in the case of the auto-oxidiser, A, opposed by the oxidisable substance, B, that the latter can be oxidised not only at the expense of the unstable

peroxide, $A\overset{\diagup O}{\underset{\diagdown O}{\cdot}}$, but also by reducing the stable oxide, A:O, we will

then have the succession of reactions:

$$A + O_2 = A\overset{\diagup O}{\underset{\diagdown O}{\cdot}}$$

$$A\overset{\diagup O}{\underset{\diagdown O}{\cdot}} + B = AO + BO$$

$$AO + B = BO + \underset{\text{regenerated}}{A}$$
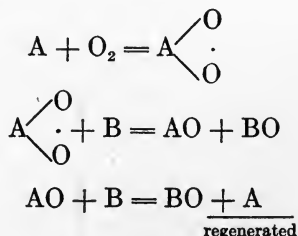
Thus the auto-oxidiser would be entirely regenerated and could again serve as a carrier of the free oxygen to the oxidisable substance. A limited amount of A could serve to oxidise an unlimited amount of B: A would then be an *oxidation catalyst.*

153. This condition is realized by cerium salts with glucose in alkaline solution. A cerium salt, dissolved in the presence of potassium carbonate, is a colorless auto-oxidiser. We have:

$$Ce(OH)_3 + O_2 + Ce(OH)_3 = \underline{Ce(OH)_3 . O . O . Ce(OH)_3}$$
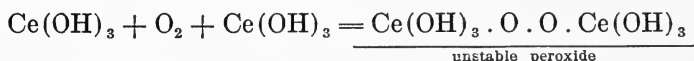
<div align="center">unstable peroxide</div>

Water reacts with this compound:

$$Ce(OH)_3 . O . O . Ce(OH)_3 + H_2O =$$
$$\underline{Ce(OH)_4} + \underline{Ce(OH)_3 . O . OH.}$$

<div align="center">ceric hydroxide   blood red</div>
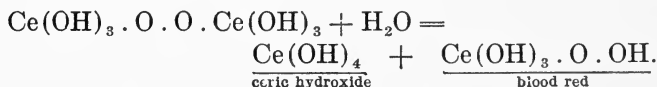
The blood-red peroxide, when brought into contact with an oxidisable substance, such as potassium arsenite, oxidises it, returning to the state of the stable yellow ceric hydrate. There has been no catalysis. But if glucose is added, the ceric hydrate oxidises the glucose, being itself reduced to cerous hydroxide which can recommence the cycle of reactions. This is catalysis.[18]

It is in this manner that small amounts of manganous salts can cause the direct oxidation of unlimited quantities of pyrogallol or hydroquinone.[19]

154. Platinum and Related Metals. The activity of platinum and related metals can be explained by a similar mechanism (243). In contact with oxygen, a sort of unstable peroxide is produced on the surface of the metal, comparable to the $A\!\!<^O_O$. of the auto-oxidisers. With an oxidisable substance, B, there is production of BO and AO, but the unstable AO oxidises another molecule of B to form BO and free A. Under these conditions the platinum would serve to render the oxygen *atomic,* and since the platinum is regenerated in the course of the reaction, the cycle can be repeated indefinitely.

The result is that the use of the platinum not only serves to lower the otherwise high temperature required by certain oxidations (*e. g.* of hydrogen or carbon monoxide) but also to realize other oxidations which can not be accomplished by *molecular* oxygen at any temperature whatsoever, for example, the liberation of iodine from potassium iodide, which is effected in the cold by aerated [20] platinum black, or

[18] Job, *Ann. Chim. Phys.,* (7), **20,** 207 (1900). *Compt. rend.,* **134,** 1052 (1902); **136,** 45 (1903).

[19] Bertrand, *Bull. Soc. Chim.,* (3), **17,** 578 and 619 (1897). Villers, *Ibid.,* (3), **17,** 675 (1897).

[20] Engler and Wöhler, *Z. anorg. Chem.,* **29,** 1 (1901).

the production of nitric acid from ammonia, by hot platinum sponge.

These fixations and liberations of oxygen take place at the surface of the metal and, for that reason, the catalytic power is proportional to the extent of that surface: it is immeasurably greater for platinum sponge, and especially for the black, than for the metal in foil or wire.

155. General Explanation of Catalysis. The idea of a temporary unstable combination has served in explaining readily the mechanism of reciprocal catalyses (146), of induced catalyses (150), and also of catalyses in the strict sense of the term, such as direct oxidations (152). This notion can be generalized and applied to all sorts of catalyses.

The formation and decomposition of intermediate compounds furnished by the catalysts usually correspond to a diminution of the free energy of the system and this diminution by steps is frequently much easier than the immediate direct diminution, somewhat as the use of a staircase facilitates a descent. Ordinarily these successive step-downs take place quite rapidly, though rapidity is not a necessary condition of catalysis.

These intermediate compounds can be isolated in a sufficiently large number of cases for us to generalize the idea and assume their formation in cases in which we can not prove their existence.

156. Catalyses in which the Intermediate Compounds can be Isolated. Berthelot has pointed out well defined examples in the decomposition of hydrogen peroxide by alkalies and by silver oxide. We will cite some other examples belonging to very different types.

Chlorination of Organic Compounds. In order to facilitate the direct chlorination of a liquid organic compound, *iodine* is dissolved in it. The chlorine unites with it to form iodine trichloride, ICl_3, which could be isolated if the iodine were alone, but which, finding itself in contact with the organic substance, gives up chlorine to it returning to the lower state of iodine monochloride which the free chlorine transforms into the trichloride, this process being repeated again and again, thus:

$$ICl_3 + MH = HCl + MCl + ICl$$
$$ICl + Cl_2 = ICl_3.$$
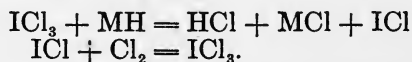
It can be proved that the chlorination is proportional to the weight of the iodine trichloride. When the operation is carried on with a continuous current of chlorine, the trichloride is constantly regenerated and we have catalysis (278).

157. The mechanism is doubtless the same for all of the *anhydrous*

metal chlorides which are used as chlorine carriers in direct chlorination (283). The intermediate products are easy to perceive in the case of the chlorides of antimony, thallium, molybdenum, etc., where several different degrees of chlorination are known of which the highest are formed by direct action of chlorine, and which give up chlorine to the organic substance, returning to the lower stages which again take up chlorine.

It is harder to see in the case of *aluminum chloride*, for which, by analogy, we must also assume a higher chloride, possibly due to the supplementary valencies of the chlorine atoms.[21]

158. Manufacture of Sulphuric Acid. The manufacture of *sulphuric acid* in the lead chamber process employs, as catalyst, nitric oxide which intimately mixed with the reacting gases (sulphur dioxide, oxygen of the air, and water vapor) serves to render rapid the reaction which would otherwise take place slowly. The production of an intermediate product is doubted by no one although there is not entire agreement as to the true nature of such compound.

159. Action of Sulphuric Acid on Alcohol. The mechanism of the action of concentrated sulphuric acid on alcohol is well known and is designated by the name of Williamson's reaction.[22] The first reaction is the production of ethyl sulphuric acid:

$$CH_3CH_2OH + H_2SO_4 = H_2O + CH_3CH_2 . O . SO_3H.$$

The latter, at 140°, reacts with a second molecule of alcohol to form ether, regenerating sulphuric acid:

$$CH_3CH_2 . O . SO_3H + CH_3CH_2OH = H_2SO_4 + (CH_3CH_2)_2O.$$

The sulphuric acid can again form ethyl sulphuric acid and so on indefinitely, since the temperature is high enough to cause the elimination of the water along with the ether. Theoretically the action should continue indefinitely: it is a well defined case of catalysis. But a portion of the sulphuric acid is reduced to *sulphur dioxide* gradually diminishing the amount of the acid.

If the mixture is heated higher, towards 160–170°, the ethyl sulphuric acid is rapidly decomposed into sulphuric acid and *ethylene:*

$$CH_3CH_2 . O . SO_3H = H_2SO_4 + CH_2 : CH_2.$$

The regenerated sulphuric acid can repeat the reaction on the alcohol and hence is a *catalyst* for the formation of ethylene from

[21] It is possible to consider this a case of the FRIEDEL and CRAFTS reaction, the aluminum chloride combining with the hydrocarbon to form an intermediate complex which reacts readily with Cl-Cl as it does with ClR. — E. E. R.

[22] WILLIAMSON, *J. Chem. Soc.*, **4**, 106, 229 and 350 (1852).

unlimited amounts of alcohol and can continue this function so long as it is not too much diminished by reduction to sulphur dioxide. This reduction is more serious in this case as the reaction temperature is higher.

160. Hydrogen Peroxide. In the catalytic decomposition of *hydrogen peroxide* by alkalies and alkaline earths, unstable intermediate compounds are plainly formed and can be isolated.[23]

The intermediate steps are equally visible in many catalyses brought about in gaseous and liquid media by solid catalysts.

161. Squibb's Method. A fine example is the method of Squibb for the preparation of acetone [24] (837).

If acetic acid vapors are passed over calcium carbonate heated to 400°, calcium acetate is produced with the liberation of carbon dioxide. If the acid is discontinued and the temperature is raised to 500°, the calcium acetate is decomposed, regenerating the carbonate and liberating acetone:

At 400° $2 \ CH_3CO_2H + CaCO_3 = CO_2 + H_2O + (CH_3CO_2)_2Ca$
At 500° $(CH_3CO_2)_2Ca = CaCO_3 + CH_3 . CO . CH_3.$
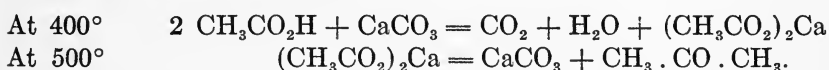
If the acetic acid is passed over the calcium carbonate at 500°, it is evident that the first reaction will tend to take place with the formation of calcium acetate, but this would decompose immediately to form acetone: the calcium carbonate would then be a catalyst (839), the reaction being:

$$2 \ CH_3CO_2H = CO_2 + H_2O + CH_3 . CO . CH_3.$$
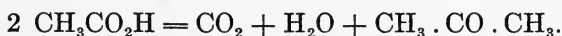
162. Catalytic Oxidation by Copper. If a current of oxygen is passed over copper heated to 250°, a layer of oxide is formed: if the vapors of an organic compound, such as an aliphatic hydrocarbon, are passed over the copper so oxidised, at the same temperature, they are immediately oxidised with the production of water, carbon dioxide, etc., and with regeneration of metallic copper. If the hydrocarbon vapors and the oxygen are sent together over the copper at the same temperature, there is production of the oxide and immediate reduction of the oxide by the hydrocarbon; the copper functions as a catalyst. The total heat of oxidation may be great enough to carry the metal, on the surface of which it is taking place, to incandescence.[25] It is easy to see that copper oxide is the intermediate step.

[23] Schöne, *Annalen*, **192**, 257 (1878) and **193**, 241 (1878). Berthelot, *Ann. Chim. Phys.*, (5), **21**, 153 (1880).

[24] Squibb, *J. Amer. Chem. Soc.*, **17**, 187 (1895) and **18**, 231 (1896). Conroy, *J. Soc. Chem. Ind.*, **21**, 302 (1902). *Rev. gén. Sc.*, **13**, 563 (1902).

[25] Sabatier and Mailhe, *Compt. rend.*, **142**, 1394 (1905).

163. Action of Nickel on Carbon Monoxide. Another example of the same kind is furnished by the destruction of carbon monoxide by nickel at 300°.

Carbon monoxide acting on reduced nickel around 100°, produces *nickel carbonyl*, $Ni(CO)_4$. This warmed to about 150° decomposes completely into carbon monoxide and nickel, while from 250° to 300°, it decomposes entirely differently, into nickel, carbon, and carbon dioxide:

$$Ni(CO)_4 = Ni + 2C + 2CO_2.$$
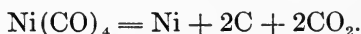
If carbon monoxide is passed over nickel at 150°, there appears to be no action since the nickel carbonyl that is formed is decomposed immediately, in place, into carbon monoxide and carbon. If the operation is carried on at 300°, there should still be the production of nickel carbonyl but it is at once decomposed into carbon dioxide, carbon, and nickel. The regenerated nickel can carry on the transformation of carbon monoxide into carbon and carbon dioxide indefinitely.

164. Catalyses in which the Intermediate Compounds can not be Isolated. In the cases given above, the intermediate products which serve as stepping-stones for the reaction can be readily observed and even isolated as well defined chemical compounds, but in more numerous cases, these intermediate steps are difficult to perceive and it is only by analogies that we can surmise their nature with more or less uncertainty.

165. Hydrogenation by Finely Divided Metals. The catalytic rôle of finely divided metals, nickel, copper, platinum, etc., in direct hydrogenation is easily explained by the assumption of unstable hydrides on their surfaces.[26] Such condensation of hydrogen actually takes place to a certain extent, as we have seen above (136), and particularly with palladium, a really definite combination takes place in the cold. This has only a feeble dissociation pressure and has been assigned the formula, Pd_3H_2, by Dewar.[27]

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[26] According to WILLSTÄTTER and WALDSCHMIDT-LEITZ (*Berichte*, **54**, 120 (1921)) oxygen must be present for hydrogenation to take place. They assume that the platinum combines with the oxygen first to form a sort of peroxide which then unites with the hydrogen:

$$Pt + O_2 \rightarrow Pt\!\!\begin{array}{c} \diagup O \\ \diagdown O \end{array} \quad \text{and} \quad Pt\!\!\begin{array}{c} \diagup O \\ \diagdown O \end{array} \cdot + H_2 \rightarrow \begin{array}{c} H \\ \diagdown \\ Pt \\ \diagup \\ H \end{array}\!\!\begin{array}{c} \diagup O \\ \cdot \\ \diagdown O \end{array}$$
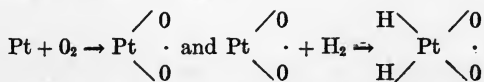
This peroxide hydride is the active intermediate compound, passing its hydrogen on to the substance to be hydrogenated and taking up more. — E. E. R.

[27] DEWAR, *Chem. News*, **76**, 274 (1897).

The hydrogen thus combined with palladium is able to produce many reactions which free hydrogen can not. It combines directly in the cold and in the dark with chlorine and with iodine as well as with oxygen.[28] It reduces chlorates to chlorides, nitrates to nitrites, ferric salts to ferrous, mercuric to mercurous, potassium ferricyanide to ferrocyanide, indigo blue to indigo white, sulphur dioxide to hydrogen sulphide, and arsenic trioxide to arsenic.[29] It transforms benzoyl chloride into benzaldehyde and nitrobenzene into aniline.[30]

166. Hydrogen occluded by platinum produces analogous effects.[31] Thus when the vapors of nitrobenzene are directed onto *platinum black* previously charged with hydrogen, all the hydrogen which is present is utilized in the production of aniline. If at this moment, more hydrogen is introduced, a new fixation takes place followed by a further reduction of nitrobenzene.

If the hydrogen and nitrobenzene vapors arrive simultaneously, there will be continuous reduction of the latter; the platinum is a hydrogenation catalyst.

The catalysis appears to be a consequence of the occlusion of the hydrogen, that is to say, of the formation of a sort of combination of the hydrogen and the metal and the use of platinum as a catalyst is advantageous since the interchange of gases is rapid with it.

Palladium, although it absorbs much more hydrogen, is usually inferior to platinum, probably because the hydrogen is not given up rapidly enough to the molecules to be hydrogenated.

167. *Copper, iron, cobalt,* and especially *nickel,* reduced from their oxides are still more advantageous, although they can retain only small amounts of free hydrogen, probably because the formation and decomposition of the hydrogen addition products are much more rapid.

With nickel, the process goes on as if there were formed, on the surface, an actual unstable hydride capable of liberating hydrogen in the *atomic* condition and consequently more active than the original molecular hydrogen. The facts lead even to the idea that there are two stages in the fixation of hydrogen such as $\frac{Ni-H}{Ni-H}$ and $Ni\big\langle^H_H$, the latter more active combination being formed by metal reduced from the oxide below 300° and capable of more kinds of work. The former, less active combination, would be produced by nickel reduced above 700°, or made from the chloride and able to hydrogenate ethy-

[28] BOETTGER, *Berichte,* **6,** 1396 (1873).

[29] GLADSTONE and TRIBE, *Chem. News,* **37,** 68 (1878).

[30] KOLBE and SAYTZEFF, *J. prakt. Chem.,* (2), **4,** 418 (1871).

[31] GLADSTONE and TRIBE, *loc. cit.* COOKE, *Chem. News,* **58,** 103 (1888).

lenic compounds, nitriles, and nitro bodies but not the aromatic nucleus.

The catalytic hydrogenation of an ethylene hydrocarbon would be represented by:

$$H_2 + Ni_2 = Ni_2H_2.$$
$$Ni_2H_2 + C_2H_4 = C_2H_6 + Ni_2.$$
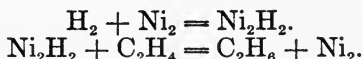
The regenerated nickel would continue indefinitely to produce this effect so long as the hydrogen and ethylene continued to arrive simultaneously.

168. If finely divided metals with free hydrogen give quickly formed and readily decomposable unstable hydrides, they should also be able to take hydrogen from substances which hold it only feebly and should be *dehydrogenation* catalysts. In general, experiment has verified this prediction (651).

169. Dehydration by Anhydrous Oxides. The dehydration of alcohols by certain oxides, as alumina, thoria, etc., can be interpreted readily by a close analogy to Williamson's reaction.

These oxides can be regarded as the anhydrides of metallic hydroxides capable of exercising the acid function, whether exclusively acid as with silicic or titanic acid, or either acid or basic (hydroxides of aluminum, thorium, chromium, etc.). Thus with alumina, the alcohol vapor would give an unstable *aluminate* which in contact with alcohol would decompose to give ether, or at a higher temperature would immediately decompose evolving ethylene; the regenerated alumina would be able to carry on this reaction indefinitely:

$$Al_2O_3 + 2C_nH_{2n+1}.OH = H_2O + Al_2O_2(OC_nH_{2n+1})_2$$

Then $\quad 2C_nH_{2n+1}.OH + Al_2O_2(OC_nH_{2n+1})_2 = 2\underset{\text{ether}}{\underline{(C_nH_{2n+1})_2O}} + Al_2O_2(OH)_2$

and $\quad Al_2O_2(OH)_2 = H_2O + Al_2O_3$

or $\quad Al_2O_2(OC_nH_{2n+1})_2 = 2\underset{\text{hydrocarbon}}{\underline{C_nH_{2n}}} + Al_2O_2(OH)_2$
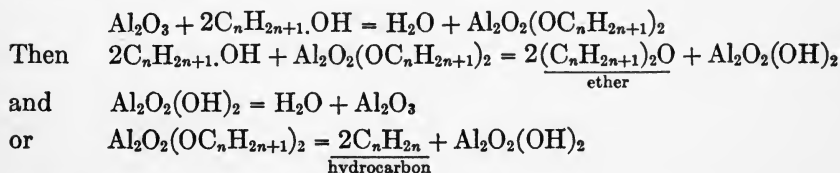
which would be immediately followed by the dehydration of the alumina.

Such alcoholates can be isolated in various ways, for example, aluminum ethylate, which is decomposed cleanly into ethylene and alumina.[32]

In the case of methyl alcohol, only the first sort of reaction is possible, but in most other cases the other takes place exclusively.[33]

170. It would be the same way with thoria which would furnish with alcohol vapors, a sort of thorium alcoholate which the heat de-

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[32] GLADSTONE and TRIBE, *Jour. Chem. Soc.*, **41**, 5 (1882).

[33] SABATIER and MAILHE, *Ann. Chim. Phys.*, (8), **20**, 349 (1910).

composes into an ethylene hydrocarbon and thoria, which is capable of reproducing the same effect indefinitely. If this is the case, this sort of *ester* would be capable of reacting chemically with various substances with which it is brought into contact and experiments have bountifully confirmed the predictions made by Sabatier and Mailhe on this point.[34]

In contact with thoria, alcohol vapors react directly with hydrogen sulphide to give *mercaptans* (743), with ammonia to form *amines* (732), with phenols to produce mixed ethers (789), and with aliphatic acids to yield *esters* (762).

171. Decomposition of Acids. In the decomposition of aliphatic acids by anhydrous oxides it is frequently easy to perceive the intermediate compound which serves as a stepping stone in the reaction; namely, the salt formed by the acid and the oxide. It appears undecomposed at temperatures lower than those used in the catalysis, as is the case with lime and zinc oxide (841). At a higher temperature the salt is immediately decomposed to form the ketone.

This intermediate formation ceases to be apparent when the acid is passed over the oxide at a higher temperature, because the formation of the salt is then balanced by its rapid destruction. For certain oxides, as *thoria* and *titania,* it can not even be perceived since, doubtless, the formation does not take place at a lower temperature than the decomposition, but the analogy is so close that we can not fail to assume similar mechanisms with all of the oxides.

172. In the decomposition of formic acid by metals or oxides (821), the intermediate compounds would be formed either from the hydrogen (passing over the metals), or from the carbon dioxide (fixed by the zinc oxide), or from the formic acid itself giving with the oxide a formate the decomposition of which would vary according to its nature. The molecule of this acid is a structure with little stability, tending to decompose in the two directions, into $CO + H_2O$ or into $CO_2 + H_2$; the affinity of the catalyst giving a transient compound, decides the direction.

173. The Friedel and Crafts Reaction. The catalytic activity of anhydrous aluminum chloride in the Friedel and Crafts reaction (884) can be explained by the production of a temporary combination between the chloride and the organic material. Thus with aromatic hydrocarbons, we would have:

$$C_6R_5H + AlCl_3 = HCl + Al\diagup\!\!\!\!\diagdown\begin{matrix}Cl_2\\C_6R_5\end{matrix}$$
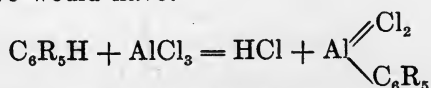
[34] SABATIER and MAILHE, *Compt. rend.,* **150**, 823 (1910).

The latter compound would react immediately on the halogen derivative present and we would have:

$$Al\big\langle{}^{Cl_2}_{C_6R_5} + R'Cl = \underset{\text{regenerated}}{AlCl_3} + R'.C_6R_5.$$
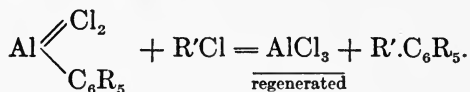
The regenerated aluminum chloride would react again with the hydrocarbon and the same reactions would be repeated. It is then a catalyst and a small amount of the salt should effect the transformation of an unlimited amount of the mixture. This is in fact what takes place in some cases where the aluminum chloride can condense a hundred times its own weight of benzene with other molecules.

174. Practically, it is often necessary to employ large amounts of the aluminum chloride, sometimes even several times the weight of the aromatic hydrocarbon. For this reason some chemists have questioned the catalytic rôle of the chloride. It is, however, not to be doubted, as the necessity of sometimes using such large amounts of the catalyst is due either to the tardiness of the reaction in some cases and the desire to hasten it by providing for the formation of a large amount of the required intermediate compound or, in other cases, to the fact that the aluminum chloride forms stable combinations with some of the reactants which withdraw a portion of it from the reaction. The reality of the formation of addition products of the aluminum chloride with the organic compounds has been established by Gustavson who has been able to isolate an addition product with benzene, an orange colored oil, $AlCl_3.3C_6H_6$, decomposable by water,[35] and in the case of the mixture of benzene and ethyl chloride, $AlCl_3.(C_2H_4)_2.3C_6H_6$, which heat dissociates into benzene and

$$Al\big\langle{}^{Cl}_{(C_2H_4Cl)_2}$$, which is stable and serves as catalyst for the transformation of the mixture.[36]

175. Action of Acids and Bases in Hydrolysis. In the decompositions by addition of water, or *hydrolyses*, such as the saponification of esters by strong mineral acids (313), or by strong bases (318), the inversion of cane sugar, the decomposition of glucosides (327), or of acetals and, inversely, in the production of esters in presence of small amounts of mineral acids (749), the active factors of the catalysis appear to be the *ions* resulting from the *electrolytic dissociation* of the acid or base.[37] The activity of the catalyst is closely

[35] GUSTAVSON, *Berichte*, **11**, 2151 (1878).

[36] GUSTAVSON, *Compt. rend.*, **136**, 1065 (1903); **140**, 940 (1905).

[37] VAN'T HOFF, *Leçons Chim. Phys.*, 1898, III, 140.

connected with the amount of this dissociation and the velocity is proportional to the number of free ions in the solution.

176. In saponifications catalyzed by soluble bases, the active factors are the *hydroxyl ions* resulting from the electrolytic dissociation of the base and we are justified in believing that the attack on the molecule of *ester*, ROA, derived from the oxy-acid AOH, is the work of the OH ions derived from the base.   Thus with caustic potash we would have:

$$\underset{\text{ester}}{ROA} + \left\{ \begin{matrix} \overline{OH} \\ + \\ K \end{matrix} \right\} = \underset{\text{alcohol}}{ROH} + \left\{ \begin{matrix} \overline{OA} \\ + \\ K \end{matrix} \right\}$$
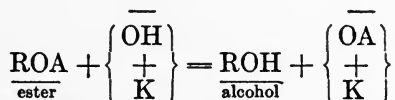
The ionized salt, AOK, is formed in the solution, but as the corresponding organic acid, AOH, is only slightly dissociated into ions, water hydrolyzes the salt to give:

$$\left\{ \begin{matrix} \overline{OA} \\ + \\ K \end{matrix} \right\} + H_2O = \underset{\text{acid}}{AOH} + \left\{ \begin{matrix} \overline{OH} \\ + \\ K \end{matrix} \right\}$$
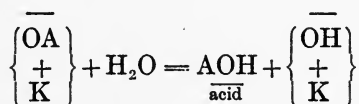
The acid, AOH, is thus liberated and the ions of the original caustic potash are free to recommence their catalytic action.

In the saponification of esters by acids it is the *hydrogen ions* that cause the effect.   Thus with hydrochloric acid, we have:

$$\underset{\text{ester}}{ROA} + \left\{ \begin{matrix} \overset{+}{H} \\ - \\ Cl \end{matrix} \right\} = \underset{\text{alcohol}}{ROH} + \left\{ \begin{matrix} \overset{+}{A} \\ - \\ Cl \end{matrix} \right\}$$
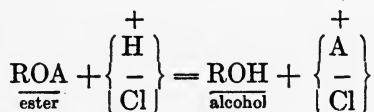
But there is immediate reaction with water to give:

$$\left\{ \begin{matrix} \overset{+}{A} \\ - \\ Cl \end{matrix} \right\} + H_2O = \underset{\text{acid}}{AOH} + \left\{ \begin{matrix} \overset{+}{H} \\ - \\ Cl \end{matrix} \right\}.$$
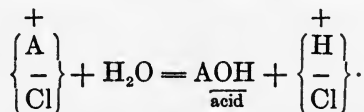
The regenerated ions of the initial molecule of hydrochloric acid can repeat the reaction and so indefinitely.   Esterification is brought about according to the same mechanism but in the inverse direction.

178. The velocity of a hydrolysis of this sort is proportional to the number of ions that are active in producing it.   With the strong acids at such dilutions that they may be regarded as completely dissociated, the effect will be independent of the nature of the acid and proportional to the concentration only.   This has been verified for hydrochloric, hydrobromic, hydriodic, nitric and chloric acids.[38]   It

[38] OSTWALD, *J. prakt. Chem.*, (2), **28**, 449 (1883).

is the same way with strong soluble bases, potassium, sodium, barium, and calcium hydroxides in sufficiently dilute solutions.[39]

179. Catalysis in general appears to be the result of purely chemical phenomena accomplished by the aid of the catalyst which gives, with one of the elements of the primitive system, a temporary unstable combination, the decomposition of which, or the reaction of which, with one of the other reactants, determines the transformation of the system, the catalyst being regenerated in its original condition and able to repeat the reaction indefinitely.

180. Ostwald has criticised the conception of the formation of intermediate compounds because it does not rest on a sufficiently exact knowledge of the reactions and because it would be further necessary to prove that the succession of reactions assumed requires less time than the direct reaction, and adds that no theory is of value in the absence of exact measurements.

To tell the truth, we do not know much more as to the true nature of the absorption of gases and vapors by porous catalysts or even by wood charcoal; this absorption, or *occlusion*, which is determined by a sort of selective affinity between the gas and the solid is a real solution penetrating to a certain depth in the solid and similar to the temporary combination which we have assumed, the differentiation of chemical and physical phenomena being always uncertain.

The theory of catalysis by means of intermediate compounds still contains many obscurities and has the fault of leaning frequently on the assumption of hypothetical intermediate products which we have not yet been able to isolate, but it is the only hypothesis that is able to explain catalysis in homogeneous solution and has the merit of applying to all cases.

As far as I am concerned, this idea of temporary unstable intermediate compounds has been the beacon light that has guided all my work on catalysis; its light may, perhaps, be dimmed by the glare of lights, as yet unsuspected, which will arise in the better explored field of chemical knowledge.[40] Actually, such as it is, in spite of its imperfections and gaps, the theory appears to us good because it is fertile and permits, in a useful way, to foresee reactions.

[39] Reicher, *Annalen*, **228**, 275 (1885). Ostwald, *J. prakt. Chem.*, (2), **35**, 112 (1887). Arrhenius, *Zeit. phys. Chem.*, **1**, 110 (1887). Bugarszky, *Ibid.*, **8**, 418 (1891).

[40] Sabatier, *Berichte*, **44**, 2001 (1911).

THEORIES OF CONTACT CATALYSIS

By WILDER D. BANCROFT

180a. For purposes of discussion the theories of contact catalysis may be grouped under three headings:—·

1. Stoichiometric theory.
2. Adsorption theory.
3. Radiation theory.

The stoichiometric theory is the one most commonly held because it involves nothing new or strange. According to this theory, one or more of the reacting substances forms with the catalytic agent a definite compound which then reacts in such a way as to give the final products. In the catalysis of hydrogen peroxide by mercury, the intermediate formation of mercuric peroxide [41] can be detected by the eye, because there is an intermittent building-up of a film which then breaks down, only to grow again. The formation of graphite is usually preceded by the formation of a carbide. The conversion of acetic acid into acetone [42] by passing the vapor over heated barium carbonate presumably involves the intermediate formation of barium acetate. In the catalytic oxidation of carbon monoxide it is usually believed that there is an alternate oxidation and reduction of the oxides which act as catalytic agents. Hydrogen peroxide is said to oxidize cobaltic oxide to peroxide and to be decomposed catalytically by cobaltic oxide.[43] Nickel peroxide reacts quantitatively with hydrogen peroxide; but the resulting oxide is not converted back into peroxide by hydrogen peroxide and consequently does not decompose it catalytically.

180b. While there are undoubtedly many cases of contact catalysis which come under this general head, it does not follow that this is the only type. It seems improbable that it would be so difficult to make carbon tetrachloride if the chlorine, which is absorbed by carbon and thereby made active,[44] were present as a definite compound of carbon and chlorine. Oxygen absorbed by charcoal will oxidize ethyl alcohol to acetic acid [45] and ethylene to carbon dioxide and water, reactions which certainly are not characteristic of any known

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[41] BREDIG and VON ANTROPOFF, *Zeit. Elektrochemie*, **12**, 585 (1906); VON ANTROPOFF, *Jour. prakt. Chem.*, (2), **77**, 273 (1908).

[42] SQUIBB, *Jour. Am. Chem. Soc.*, **17**, 187 (1895).

[43] BAYLEY, *Phil. Mag.*, (5), **7**, 126 (1879).

[44] DAMOISEAU, *Compt. rend.*, **73**, 60 (1876).

[45] CALVERT, *Jour. Chem. Soc.*, **20**, 293 (1867).

oxide of carbon. It is very important that we should decide in each particular case whether a definite intermediate compound is formed and, if so, what compound. Only in this way can we escape from the haziness which handicaps so much of the work on catalysis. For instance, it seems obvious to account for the hydrogenating power of pulverulent nickel by postulating the formation of an unstable hydride; but the recent work of Professor Taylor of Princeton shows that no hydride is formed. It is easy to account for the different action of nickel, thoria, and titania on ethyl acetate by postulating the formation of intermediate compounds; but there is no experimental evidence that these hypothetical compounds would break down in the desired way if formed. To this day people are not agreed as to what intermediate compound is formed in the Deacon chlorine process.

180c. The absorption theory does not postulate the intermediate formation of definite chemical compounds. The assumption is that the absorption of the substances to be catalyzed makes them more active chemically. This may occur in different ways. Since the reaction velocity is a function of the concentration, it was natural to ascribe the catalysis of oxyhydrogen gas by platinum to the increased concentration at the surface of the metal. This seems to have been disproved by the recent experiments in which oxyhydrogen gas is reported to be quite stable in presence of an alkaline solution when under a pressure of three thousand atmospheres. This explanation will not suffice to account for the cases in which the same substance decomposes in one way in presence of one catalytic agent and in another way in presence of another. On the other hand, the increase in concentration must have an effect in some cases and it seems probable that this could be found most easily if one studies a reaction which takes place at a measurable rate in the absence of a catalytic agent, say ester formation, and if one takes an extremely non-specific absorbent, such as Patrick's silica gel.

180d. Langmuir [46] considers that an adsorbed gas is held chemically by the unsaturated valences at the surface of the solid, thus forming a new type of compound which I have called indefinite compounds because they are not of the ordinary type and because no definite formulas can be written for them. In the case of the adsorption of argon by charcoal, for instance, we should have to write C_xAr_y where x varies with the mass of the charcoal and y with its surface as well as with the pressure and temperature. Chemical reactions may take place either between adjacent atoms

[46] *Jour. Am. Chem. Soc.*, **37**, 1139 (1915); **38**, 1145 (1916).

on the surface or when gas molecules strike molecules or atoms on the surface. So far as the catalytic part is concerned this is much the same as the view of Debus.[47] " If now a piece of platinum is placed in peroxide of hydrogen, the molecules of the latter will place themselves in such a position on the surface of the platinum that one oxygen atom of the peroxide is turned towards the platinum and as near to it as possible. The peroxide is polarized. But this has the effect also of bringing the oxygen atoms of different molecules of peroxide in such close proximity on the surface of the metal that they can combine to form common oxygen, the decomposition of the peroxide into water and oxygen and the development of energy being the consequence. The action of the platinum places the molecules of the peroxide in the *position of reaction* towards each other."

180e. Langmuir has contemplated the possibility of a reaction between two adsorbed molecules and between one adsorbed and one free molecule. The second case is one in which a more effective collision is produced. This is a perfectly legitimate hypothesis. According to the kinetic theory the reaction velocity is proportional to the number of collisions between possibly reacting molecules; but it does not follow at all that two molecules react every time they collide. If a large number of collisions is necessary on an average before a pair of molecules react, anything which would make these collisions more helpful might increase the reaction velocity enormously. The first question is then whether there is any evidence of ineffective collisions. This matter has been studied by Strutt[48] who comes to the conclusion that a molecule of ozone reacts every time it strikes a molecule of silver oxide; but that a molecule of active nitrogen collides with a molecule of copper oxide five hundred times on an average before they react, while two molecules of ozone at 100° collide on an average 6×10^{11} times before they react. Without insisting on the absolute accuracy of these figures there is evidently plenty of margin for an increase in reaction velocity with ozone at 100° if one could produce more effective collisions. Langmuir[49] finds that, at a pressure of not over 5 bars, and at 2770° K, 15% of all oxygen molecules striking a tungsten filament react with it to form tungstic oxide, WO_3. This coefficient increases at higher temperatures and at 3300° K about 50% of all the oxygen molecules which strike the filament react with it to form tungstic oxide.

[47] *Jour. Chem. Soc.*, **53**, 327 (1888); Cf. Hüfner, *Jour. prakt. chem.*, (2), **10**, 385 (1874).

[48] *Proc. Roy. Soc.*, **87**, A, 302 (1912).

[49] *Jour. Am. Chem. Soc.*, **35**, 105 (1913); **38**, 2270 (1916).

180f. It is possible that a catalytic agent may cause one molecule to strike another amidships instead of head-on and may thereby increase the effectiveness of the collisions. It is not impossible that part, at least, of the effect of solvents on reaction velocity may be due to some such thing as this. If we adopt the views of Debus and Langmuir on oriented adsorption, all sorts of things become possible. If ethyl acetate, for instance, attaches itself to one adsorbent by the methyl group, to another by the ethyl group, and to a third by the carboxyl group, it might very well be that bombardment of the captive molecule by free ones might lead to very different reaction products in the three cases. Such a suggestion is of very little value, however, unless it can be made definite. We do not know as yet whether ethyl acetate is actually adsorbed in one way by nickel, in another way by thoria, and in a third way by titania, nor do we know whether the difference in the manner of adsorption, assuming it to occur, is of such a nature as to account for the differences in the reaction products.

180g. It is possible not to make an assumption as to the precise way in which adsorption takes place and merely to consider the surface of the solid as acting like a solvent. If the chemical potential of a possible reaction product is lowered in any way, there is an increased tendency for that reaction product to form.[50] If one treats a substance with a dehydrating agent, the tendency to split off water is increased. If a substance like alcohol can react in two different ways, we should expect a given catalytic agent to accelerate the reaction producing the reaction products which are adsorbed the most strongly by that catalytic agent.[51] This appears to happen in the simpler cases. Ipatief [52] states that the decomposition of alcohol into ethylene and water in presence of heated alumina is due to the taking up of water by the alumina. That alumina takes up water very strongly was shown by Johnson,[53] who found that up to a certain point alumina adsorbs water vapor as completely as does phosphorus pentoxide. Sabatier attributed the decomposition of alcohol into acetaldehyde and hydrogen in presence of pulverulent nickel to the tendency to formation of a nickel hydride. Both he and Ipatief assume the formation of definite compounds; but the argument is just as strong in case we postulate that the catalytic agent adsorbs the reaction products strongly instead of combining with them. An

[50] Miller, *Jour. Phys. Chem.*, **1**, 636 (1897).
[51] Bancroft, *Jour. Phys. Chem.*, **21**, 591 (1917).
[52] *Berichte*, **37**, 2986 (1904).
[53] *Jour. Am. Chem. Soc.*, **34**, 911 (1912).

excess of the adsorbed reaction product should cut down the rate of reaction and that is the case. When working at high pressures, the first stage in the dehydration of alcohol in presence of heated alumina is the production of ether. When an equimolecular mixture of ether and water is passed over alumina at 400°, practically no ethylene is formed.[54] Engelder [55] showed that presence of water vapor decreased very markedly the rate of decomposition of ethyl alcohol by alumina. Titania causes alcohol to split both into acetaldehyde and hydrogen and into ethylene and water. Engelder showed that addition of hydrogen to the alcohol vapor increased the relative yield of ethylene and addition of water vapor increased the relative yield of acetaldehyde, though the difference was not as marked as one might have wished. A somewhat similar result appears to have been obtained unconsciously by Berthelot [56] fifty years ago. He heated formic acid at 260° without any specified catalytic agent and found that when only a third of the formic acid is decomposed the reaction appears to be

$$HCO_2H = CO + H_2O.$$
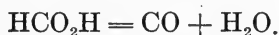
If all the formic acid is decomposed, the reaction is approximately

$$2\ HCO_2H = CO + H_2O + CO_2 + H_2.$$
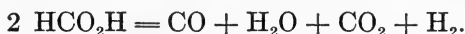
This unexpected result can only be true in case the reaction

$$HCO_2H = CO_2 + H_2$$
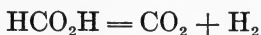
predominates during the latter part of the decomposition and this can happen only in case the original decomposition products check the initial reaction and thus permit the second reaction to come to the fore. The experiments by Berthelot should be repeated so as to make sure that they are right and that the suggested explanation is the true one.

180h. While this seems very satisfactory, there are certain points which must not be overlooked. When making ethylene at Edgewood Arsenal during the war, it was found advisable to have a large amount of steam present with the alcohol vapor in order to make temperature regulation easier. This undoubtedly decreased the rate of decomposition of the alcohol; but that difficulty was overcome by working at a higher temperature. I find it very difficult to see how alumina can dehydrate alcohol in presence of a large amount of water vapor if the reason the alumina acts is because of its strong adsorption of water vapor. In spite of the fact that the theory of the selective

[54] IPATIEF, *Berichte*, **37**, 2996 (1904).
[55] *Jour. Phys. Chem.*, **21**, 676 (1917).
[56] *Ann. Chim. Phys.*, (4), **18**, 42 (1869).

adsorption of the reaction products undoubtedly contains a great amount of truth, it must be admitted that, as now formulated, it is not the final word. It must be modified before it can be considered as satisfactory. If it breaks down temporarily in the simple case of the decomposition of alcohol, it is not surprising that we cannot as yet predict the decompositions of the esters by means of it.

180i. The whole problem of catalysis has been put in a general but vague form by Baly and Krulla and Baly and Rice [57] who consider that we have a partial conversion of one or more reacting substances into active forms through opening up fields of force by the rupture of normal valence or of contra-valences. The trouble with this is that it is as yet too vague to be of much value as a working hypothesis, though it makes an admirable starting-point. Methods must be devised for showing in each particular case what particular valences or contra-valences are ruptured as a preliminary step in the reaction.

180j. The radiation theory postulates that the catalytic agent emits radiations which convert one or more of the reacting substances into active modifications. Miss Woker [58] has given a sketch of the earlier speculations as to radiation. The only one which has survived is that of Barendrecht,[59] and his calculations have been criticized severely by Henri.[60] Krüger [61] has attempted to account for a number of phenomena in homogeneous solutions by postulating infra-red radiation. This idea has been developed by W. C. McC. Lewis [62] and applied to the change of reaction velocity with the temperature and to contact catalysis. More recently, Perrin [63] has put forward similar views without making any reference to the work of others. Lewis believes that the catalytic agents emit infra-red rays which activate the reacting substance. This would seem to make it possible for a catalytic agent to act at a distance; but this difficulty can be avoided by assuming that the intensity of the infra-red radiation is so low that it is effective only when the distances are molecular. An interesting case comes up in homogeneous solu-

[57] *Jour. Chem. Soc.,* **101**, 1469, 1475 (1912).

[58] *Die Katalyse,* p. 60 (1910).

[59] *Zeit. phys. Chem.,* **49**, 456 (1904); **54**, 367 (1906); *Proc. Kon. Akad. Wet. Amsterdam,* **22**, 29 (1919).

[60] *Zeit. phys. Chem.,* **51**, 19 (1905).

[61] *Zeit. Elektrochemie,* **17**, 453 (1911).

[62] *Jour. Chem. Soc.,* **105**, 2330 (1914); **107**, 233 (1915); **109**, 55, 67, 796 (1916); **111**, 457, 1036 (1917); **113**, 471 (1918); **115**, 182 (1919); *System of Physical Chemistry,* **3**, 138 (1919).

[63] PERRIN, *Ann. Physique,* (9), **11**, 5 (1919).

tions. Methyl acetate has a strong absorption band between $5\,\mu$ and $11\,\mu$ the hydrogen ion is supposed to emit wave-lengths over the range $1.1–11\,\mu$, and hydrogen ion catalyzes methyl acetate solutions. Professor Rideal of the University of Illinois has shown that infra-red radiations corresponding to the absorption band of methyl acetate do accelerate the reaction between methyl acetate and water; but this would happen on any hypothesis. It has not been shown that the catalytic action of the infra-red rays supposed to be emitted by hydrogen ion corresponds quantitatively with the catalytic action of the hydrogen ion. This might be a difficult thing to establish to the satisfaction of the doubters; but there is a test which would probably be accepted as crucial by everybody. Heated nickel decomposes ethyl acetate into propane and carbon dioxide; heated thoria converts it into acetone, ethyl alcohol, ethylene and carbon dioxide; while heated titania changes it into acetic acid and ethylene.[64] If somebody would produce these three sets of reactions separately by means of infra-red radiations with no catalytic agent present, the radiation theory would have a standing which it does not have at present. Since alumina is very permeable to infra-red radiations and ferrous oxide is not,[65] the latter should be a very efficient catalytic agent according to the radiation theory. This has not been tested so far as I know. Tyndall[66] states that gum arabic is practically impermeable to infra-red radiations. If this is true, gum arabic should catalyze the hydrolysis of methyl acetate enormously if the radiation theory is sound.

180k. This brief sketch of the theories of contact catalysis shows how unsatisfactory our present knowledge is. This is due to the inaccurate and incomplete way in which the single reactions have been studied. We do not know which cases involve definite intermediate compounds and which do not. When we are agreed that definite intermediate compounds are formed, we do not agree as to their nature. We talk about breaking normal valences or contra-valences; but we do not specify which valences or which contra-valences. When ethyl alcohol is decomposed by pulverulent nickel into acetaldehyde and hydrogen, does molecular hydrogen split off or do the two hydrogens come off separately? If the latter happens does the first hydrogen come from the hydroxyl group or not? When ethyl alcohol is decomposed by alumina into ethylene and water, does water, hydrogen, or hydroxyl come off first? It can hardly be water because it is possible to stop the reaction at the intermediate stage of ether,

[64] Sabatier and Mailhe, *Compt. rend.,* **152,** 669 (1911).

[65] Zsigmondy, *Dingler's Polytech. Jour.,* (6), **37,** 17, 68, 108; **39,** 237 (1893).

[66] *Fragments of Science: Radiant Heat and its Relations.*

and it is probably not monatomic hydrogen because that is what happens with nickel. If the first stage is a splitting off of hydroxyl, does the other hydrogen come from the adjacent carbon atom giving ethylene direct or does it come from the same carbon atom, forming a substituted methylene, CH_3CH, which then rearranges to ethylene? The decomposition of ether by alumina apparently must lead to $2\ CH_3CH + H_2O$ as one of the intermediate stages. How does nickel decompose ether?

180l. In at least two instances it should be relatively simple to determine the reacting radicals. If we pass a mixture of ethyl acetate and hydrogen over pulverulent nickel, it is probable that some or all of the initial products will be reduced before they have time to react in the normal way. A study of the reaction products will therefore throw light on the probable mechanism of the reaction which occurs in the absence of hydrogen. If we obtained CH_4 and $HCO_2C_2H_5$, for instance, we should conclude that the original break had been into CH_3 and $CO_2C_2H_5$. If we found CH_3CO_2H and C_2H_6, we should conclude that these were reduction products of CH_3CO_2 and C_2H_5. If the reaction products were CH_4, C_2H_6, and CO_2 or some reduction product of this last, we should undoubtedly assume that ethyl acetate splits simultaneously into CH_3, CO_2 and C_2H_5.

180m. If ether is passed over pulverulent nickel, the dissociation will probably be to $C_2H_5O + C_2H_5$ or to $C_2H_5O + C_2H_4 + H$. In the first case the final products will be $2\ C_2H_4$ and H_2O just as with alumina. In the second case they are likely to be $CH_3CHO + C_2H_4 + H_2$, though the ethylene and hydrogen may combine more or less completely to form ethane.

180n. These two illustrations are sufficient to indicate the kind of work that ought to be done and the organic chemists will undoubtedly be able to develop this suggestion in most unexpected ways.

The following cases are worth considering, though it must not be assumed that the reactions run as written for one hundred per cent yield.

With nickel we get the following decompositions of the esters:

$$CH_3CO_2CH_2CH_3 = CH_3CH_2CH_3 + CO_2$$
$$CH_3CO_2CH_3 = CH_3CH_3 + CO_2$$
$$HCO_2CH_3 = CH_4(?) + CO_2$$
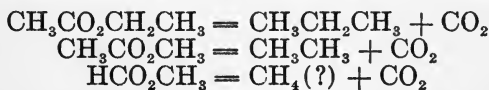
With thoria the decomposition is quite different:

$$2\ CH_3CO_2CH_2CH_3 = CH_3COCH_3 + CO_2 + (C_2H_5)_2O$$
$$= CH_3COCH_3 + CO_2 + C_2H_5OH + C_2H_4$$
$$2\ CH_3CO_2CH_3 = CH_3COCH_3 + CO_2 + (CH_3)_2O$$
$$2\ HCO_2CH_3 = HCHO + CO_2 + (CH_3)_2O$$
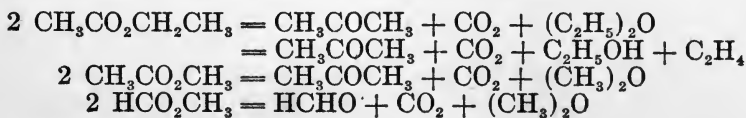
With titania there is a third set of products:

$$CH_3CO_2CH_2CH_3 = CH_3CO_2H + C_2H_4$$
$$2\ CH_3CO_2CH_3 = 2CH_3CO_2H + C_2H_4$$
$$HCO_2CH_3 = HCO_2H + CH_2 = CO + CH_3OH.$$
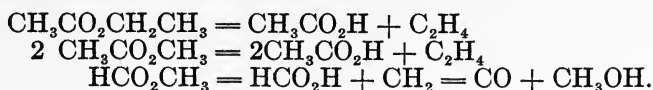
The decompositions are regular and characteristic with each catalytic agent and the molecules must break or slip at different points in the different cases. It would help a great deal towards formulating a theory of the behavior of these oxides if we knew exactly what happened in each case. Of course, a study of this sort should include the chlorinated esters. There is some evidence to show that the decomposition may shift from one type to another with increasing substitution of hydrogen by chlorine.

180o. While we have no satisfactorily developed theories of contact catalysis at present, our theoretical knowledge in regard to the poisoning of catalytic agents is in good shape, though it is not supported as yet by adequate experimental evidence. Since the reaction takes place in or at the surface, it follows that any substance, which cuts down the rate at which the reacting substances reach the catalytic surface [67] or which prevents them from reaching it, will decrease the reaction velocity and may destroy the catalytic action entirely. Berliner [68] has shown that traces of fatty vapors from the air or from the grease on the stop-cocks will decrease the adsorption of hydrogen by palladium from nearly nine hundred volumes practically to nothing. Faraday [69] has shown that traces of grease destroy the catalytic action of platinum on oxyhydrogen gas. De Hemptinne [70] has apparently shown that carbon monoxide cuts down the adsorption of hydrogen by palladium, though his method of presenting his results is very obscure. Harbeck and Lunge [71] found that carbon monoxide inhibits practically completely the catalytic action of platinum on a mixture of ethylene and hydrogen. Schönbein [72] pointed out that the hydrides of sulphur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the catalytic action of platinum on mixtures of air with hydrogen or ether. He considered that the hydride must decompose, giving rise to a solid film. This is not necessary in order to account for the phenomenon; but he seems to have been right in at least one case, for Maxted [73] has found that

[67] TAYLOR, *Trans. Am. Electrochem. Soc.,* **36** (1919).

[68] *Wied. Ann.,* **35,** 903 (1888).

[69] *Experimental Researches on Electricity,* **1,** 185 (1839).

[70] *Zeit. phys. Chem.,* **27,** 249 (1898).

[71] *Zeit. anorg. Chem.,* **16,** 50 (1898).

[72] *Jour. prakt. Chem.,* **29,** 238 (1843).

[73] *Jour. Chem. Soc.,* **115,** 1050 (1919).

hydrogen sulphide is decomposed by platinum black with evolution of hydrogen, and that the platinum then does not adsorb hydrogen. Paal and Hartmann [74] state that the catalytic action of palladium hydrosol and its adsorption of hydrogen are destroyed by metallic mercury or by the oxide of mercury.

180p. Langmuir [75] believes that oxygen prevents dissociation of hydrogen by a heated tungsten filament because it cuts down the adsorption of the hydrogen.

180q. Harned [76] has shown that the rate of adsorption [77] of chlorpicrin by a charcoal which has been cleaned by washing with chlorpicrin is much greater at first than by a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium. Taylor points out that normally the time of contact between a gas and the solid catalytic agent is extremely small and consequently anything which decreases the rate of adsorption will cut down the reaction velocity very much.

180r. It is easy to see that the piling up of the reaction products will cut down the reaction velocity, if they prevent the reacting substances from coming in contact with the catalytic agent. Bunsen apparently recognized this as early as 1857 for he is quoted [78] as saying that it is only when the products of decomposition are removed and new matter is brought into contact that the reaction continues. This has been observed experimentally in the contact sulphuric acid process.[79] The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink,[80] who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperature, Henry [81] recognized that the presence of the reaction product might slow up the rate of reaction and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks

[74] *Berichte,* **51,** 711 (1918).

[75] *Jour. Am. Chem. Soc.,* **38,** 2272 (1916).

[76] *Jour. Am. Chem. Soc.,* **42,** 372 (1920).

[77] TAYLOR, *Trans. Am. Electrochem. Soc.,* **36** (1919).

[78] DEACON, *Jour. Chem. Soc.,* **25,** 736 (1872).

[79] BODLÄNDER and KOPPEN, *Zeit. Elektrochemie,* **9,** 566 (1903); BERL, *Zeit. anorg. Chem.,* **44,** 267 (1905).

[80] BODENSTEIN and FINK, *Zeit. phys. Chem.,* **60,** 61 (1907).

[81] *Phil. Mag.* (3), **9,** 324 (1836).

the catalytic dehydration of ether [82] and of alcohol [83] and hydrogen cuts down the catalytic dehydrogenation of alcohol.

180s. When catalytic poisons are present or are formed during the reaction, the apparent equilibrium may vary with the amount of the catalytic agent.[84] With only a small amount present, the catalytic agent will be poisoned before the reaction has run very far. In the hydrolysis of ethyl butyrate by enzymes, the reaction apparently runs to different end-points depending on the relative amounts of enzyme.[85]

While our theoretical knowledge in regard to the poisoning of catalytic agents is fairly adequate, we know literally nothing except empirically in regard to the action of the so-called promoters. It has recently been found that the addition of small amounts of a substance which does not in itself have any very marked catalytic action may make the catalyst considerably more active. Such substances were called promoters in the patents of the *Badische Anilin and Soda Fabrik,* and the term is now in common use. Rideal and Taylor say: " Thus far no theory put forward to account for the acceleration of reaction by minute quantities of promoters added to the main catalyst material is completely satisfactory. A possible mechanism, which, however, has received no experimental test, may be advanced by considering the case of ammonia synthesis from mixtures of nitrogen and hydrogen. Reduced iron is an available contact substance, the activity of which may be regarded as due to the simultaneous formation of the compounds, hydride and nitride, with subsequent rearrangement to give ammonia and unchanged iron. Or, maybe, the activity of the iron is due to simultaneous adsorption of the two gases. The particular mechanism of the catalysis is unimportant for the present considerations. Now such bodies as molybdenum, tungsten, and uranium have been proposed, among others, as promoters of the activity of iron. It is conceivable that these act by adjusting the ratio in which the elementary gases are adsorbed by or temporarily combined with the catalytic material to give a ratio of reactive nitrogen and hydrogen more nearly that required for the synthesis, namely, one of nitrogen to three of hydrogen. From the nature of the materials suggested as promoters, it would seem that they are in the main nitride-forming materials, which on the above assumption of mechanism would lead to the conclusion that the original iron tended

[82] IPATIEF, *Berichte,* **37,** 2996 (1904).
[83] LEWIS, *Jour. Chem. Soc.,* **115,** 182 (1919).
[84] BANCROFT, *Jour. Phys. Chem.,* **22,** 22 (1918).
[85] KASTLE and LOEVENHART, *Am. Chem. Jour.,* **24,** 491 (1900).

to adsorb or form an intermediate compound with a greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The catalytic activity of reduced iron as a hydrogenation agent would tend to confirm this viewpoint.

180t. " In reference to this suggested mechanism it must be emphasized, however, that in such examples of ' promotion,' as require only minute quantities of added promoter the activity is more difficult to understand. With the case of ammonia synthesis, the promoters are added in marked concentrations. It is difficult to realize, however, that 0.5 per cent of ceria or a concentration of one molecule of ceria among 200 molecules of iron oxide, in the example cited above in reference to catalytic hydrogen production, can so far ' redress the balance ' of adsorption or combination as to produce the marked increase in activity of which it is capable. It is obvious that in this phase of the problem there lies an exceedingly fascinating field for scientific investigation, with the added advantages that, being practically virgin territory, the harvest to be gained therefrom should be rich and abundant."

180u. Instead of the promoter changing the ratio of adsorption, it might be that the catalytic agent activates only one of the reacting agents or activates one chiefly, and that the promoter activates the other. Thus it might be, in the ammonia synthesis, that iron activates the hydrogen chiefly so that we have hydrogenation of the nitrogen. The molybdenum might tend to activate the nitrogen giving rise to nitridation of hydrogen, or it might increase the activation of the nitrogen. Such a state of things is not impossible theoretically. When a dye reacts with oxygen under the influence of light, the light may make the oxygen active, in which case the activated oxygen oxidizes the dye, or the light may make the dye active in which case the activated dye reduces the oxygen. It is easy to decide this question by seeing whether the effective light corresponds to an adsorption band for the dye or for the oxygen.

CHAPTER IV

ISOMERIZATIONS, POLYMERIZATIONS, AND CONDENSATIONS BY ADDITION

§ 1. ISOMERIZATIONS

181. ISOMERIZATIONS, that is to say, changes of structure effected within a molecule without modifying its composition, are often accomplished by the action of heat alone.

As catalysts have frequently the effect of lowering the temperature of reactions, it can be foreseen that their use will permit, in many cases, of realizing an isomerization at a lower temperature, or causing it to go more rapidly. Experiment has often verified this prediction under very varied conditions.

Strong mineral acids bring about a large number of isomerizations; the concentration of the acid has usually a great influence on the direction of the transformation. The mechanism of the change can usually be interpreted by assuming the addition of water to the original compound under the influence of the acid ions followed by a dehydration, or the reverse.

182. Change of Geometric Isomers. The transformation of *fumaric acid* into *maleïc* is brought about by a large number of catalysts, for example *hydrobromic* or *hydriodic acids* in hot concentrated solution,[1] hot *hydrochloric acid*,[2] or hot dilute *nitric acid*.[3]

Bromine acts, in the cold, on maleïc acid to give dibromsuccinic acid but, at the same time, a part of the maleïc acid is changed to fumaric.[4]

Likewise, traces of *iodine* are sufficient to transform maleïc esters into fumaric.[5]

If to a solution of maleïc acid an equivalent amount of *sodium thiosulphate* be added and then sulphuric acid, sulphur dioxide is evolved without appreciable separation of sulphur and 25% of fumaric acid crystallizes out.[6]

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[1] KEKULÉ, *Annalen, Supp. Band,* **1**, 133 (1861).
[2] KEKULÉ and STRECKER, *Annalen,* **223**, 186 (1884).
[3] KEKULÉ, *Annalen, Supp. Band,* **2**, 93 (1862).
[4] PETRI, *Annalen,* **195**, 49 (1879).
[5] SKRAUP, *Monatsh.,* **12**, 107 (1891).
[6] TANATAR, *J. Russian Phys. Chem. Soc.,* **43**, 1742 (1912), *C. A.,* **6**, 1279.

When *hydrogen sulphide* is passed into solutions of lead, copper, or cadmium maleates, the maleïc acid set free is changed to fumaric.[7]

183. *Citraconic acid* warmed with dilute *nitric acid*,[8] or with concentrated *hydrobromic acid*,[9] or with concentrated *hydriodic acid*,[10] is changed into *mesaconic* acid.

Warmed above 100° with a concentrated solution of caustic soda, it gives mesaconic acid with a little *itaconic*.[11]

Itaconic acid dissolved in a mixture of ether and chloroform to which a few drops of a chloroform solution of bromine have been added, and exposed to sunlight, is transformed into mesaconic acid.[12]

Itaconic acid boiled with soda lye changes, almost entirely, into mesaconic.[13]

184. Small amounts of *nitrous acid* transform a number of *cis ethylenic* acids into their *trans isomers*, *oleïc* into *elaïdic*,[14] *hyprogaeic* into *gaïdic*,[15] *erucic*, $C_8H_{17}CH : CH(CH_2)_{11}CO_2H$, into *brassidic*.[16]

185. *α-Benzaldoxime* in contact with *hydrogen chloride* or with crystallized *pyrosulphuric* acid is changed into   *β-benzaldoxime*.[17] The reverse change is brought about by contact with dilute *sulphuric acid*.

186. **Changes of Optical Isomers.**   Solutions of caustic soda can determine numerous stereo-isomeric changes in the sugar group and the same is true of solutions of lime and baryta and even of pure water mixed with lead and zinc hydroxides.[18]   *Glucose, mannose* and *fructose,* heated two hours under these conditions yield the same mixture of these three hexoses.   In the cold and with concentrated alkalies, the same isomerization takes place in five days.   In the same way, *galactose* gives a mixture of *sorbose, tagatose, talose* and *galtose*.[18]   Similarly baryta water transforms *gulose* or *idose* into *sorbose*.[19]

[7] Skraup, *loc. cit.*

[8] Gottlieb, *Annalen,* **77**, 268 (1857).

[9] Fittig, *Ibid.,* **188**, 77 and 80 (1877).

[10] Kekulé, *Ibid., Supl.,* **2**, 94 (1862).

[11] Delisle, *Ibid.,* **269**, 82 (1892).   Fittig and Langworthy, *Ibid.,* **304**, 152 (1899).

[12] Fittig and Langworthy, *Ibid.,* **304**, 152 (1899).

[13] Fittig and Köhl, *Ibid.,* **305**, 41 (1899).

[14] Boudet, *Ann. Chim. Phys.* (2), **50**, 391 (1832).   Laurent, *Ibid.* (2), **65**, 149 (1837).

[15] Caldwell and Gössmann, *Annalen,* **99**, 307 (1856).

[16] Haussknecht, *Ibid.,* **143**, 54 (1867).

[17] Beckmann, *Berichte,* **20**, 2766 (1887).

[18] Lobry de Bruyn and Van Ekenstein, *Rec. Trav. Chim. Pays-Bas,* **14**, 203 (1895) and **15**, 92 (1896).

[19] Van Ekenstein and Blanksma, *Ibid.,* **27**, 1 (1908).

187. The acids derived from the hexoses are isomerized when they are heated to 135–150° with an organic base that does not yield amides with the acids; quinoline or pyridine are usually employed. The new acid differs from the old only in the arrangement of the groups around the last asymmetric carbon atom. Furthermore, the isomerizations take place in both directions, reaching the same limit. Thus *gluconic* acid furnishes *mannonic* with quinoline and reciprocally.[20]   Likewise with pyridine we pass from *arabonic* acid (with five carbon atoms) to *ribonic*,[21] from *lyxonic* to *xylonic*,[22] and also from the dibasic acid, *talomucic*, to *mucic*.[23]

188. The sugars, glucose, laevulose, galactose, arabinose, and xylose, which are not susceptible of a molecular decomposition by the addition of water, present a special phenomenon known as *multirotation;* the rotatory power observed immediately after solution in water is much greater than that after some time.[24]

Thus the rotation of glucose starts at 105° and goes down to half of this, 52.5°.[25]   The explanation is that there are isomeric molecular modifications of these various sugars, analogous to the three varieties that Tanret has been able to isolate for glucose.[26]

Of the three varieties, the one that is stable in dilute solution, called β, has exactly the rotatory power finally found, 52.5°, another form α has the value 106°. The passage to the stable isomer takes place slowly in the cold, rapidly when hot, but is greatly accelerated by the presence of *mineral acids*.[27]

189. *d.Menthone* on long contact with *sulphuric acid* containing 10% of its volume of water passes to *l.menthone*.[28]

190. **Migrations of Double and Triple Bonds.** *Isopropylethylene,* $(CH_3)_2CH \cdot CH : CH_2$, when heated under pressure at 480–500° in the presence of anhydrous *alumina,* is transformed into *trimethyl-ethylene,* $(CH_3)_2C : CH \cdot CH_3$.[29]

191. *Eugenol,* when boiled with amyl alcoholic potash, changes to *isoeugenol,* the direct oxidation of which furnishes vanilline: [30]

[20] E. Fischer, *Berichte,* **23**, 801 (1890).

[21] Fischer and Piloty, *Berichte,* **24**, 4216 (1891).

[22] Fischer and Bromberg, *Berichte,* **29**, 584 (1896).

[23] Fischer and Morell, *Berichte,* **27**, 387 (1894).

[24] Dubrunfaut, *Ann. Chim. Phys.* (3), **18**, 105 (1846).

[25] Parcus and Tollens, *Annalen,* **257**, 160 (1890).

[26] Tanret, *Bull. Soc. Chim.* (3), **15**, 195 and 349 (1896).

[27] Erdmann, *Jahresb.,* **1855**, 672.

[28] Beckmann, *Annalen,* 250, 334 (1889).

[29] Ipatief, *J. Russian Phys. Chem. Soc.,* **38**, 63 and 92 (1906), *C.,* **1906**, (2), 86 and 87.

[30] Tiemann, *Berichte,* **24**, 2871 (1891).

$$\underset{\underset{OH}{\diagdown}}{\overset{\overset{CH_2 \cdot CH:CH_2}{\diagup}}{C_6H_3 - OCH_3}} \quad \rightarrow \quad \underset{\underset{OH}{\diagdown}}{\overset{\overset{CH:CH \cdot CH_3}{\diagup}}{C_6H_3 - OCH_3}}$$
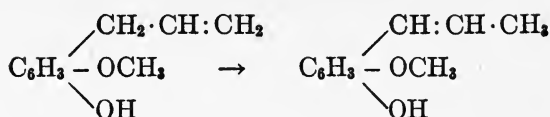
192. The acetylene triple bond undergoes analogous transpositions under the influence of *sodium* or of *alkalies*.

Ethyl-acetylene, $CH_3 \cdot CH_2 \cdot C \vdots CH$, heated with potash to 170°, changes to *dimethyl-acetylene*, $CH_3 \cdot C \vdots C \cdot CH_3$.[31]

Inversely, disubstituted acetylene hydrocarbons are changed into true acetylenes when they are heated with sodium, a part of the new hydrocarbon combining with the metal, e. g. *methyl-ethyl-acetylene*, $CH_3 \cdot C \vdots C \cdot CH_2 \cdot CH_3$, gives *propyl-acetylene*, $CH_3 \cdot CH_2 \cdot CH_2 \cdot C \vdots CH$.[32]

The same catalysts cause the transformation of allenic hydrocarbons into acetylene hydrocarbons and inversely. Thus *diethyl-allene*, $CH_3 \cdot CH_2 \cdot CH : C : CH \cdot CH_2 \cdot CH_3$, which under the influence of heat alone isomerizes into *methyl-ethyl-butadiene*, is changed by contact with metallic sodium into *diethyl-allylene*, $CH_3 \cdot CH_2 \cdot CH_2 \cdot C \vdots C.CH_2.CH_3$.[33]

Inversely *isopropyl-acetylene*, $(CH_3)_2CH \cdot C \vdots CH$, heated above 150° with alcoholic potash, changes to *dimethyl-allene*, $(CH_3)_2C \colon C : CH_2$.[34]

193. **Decyclizations.** *Cyclo-propane* is not changed to propylene by heat alone below 600°, but in the presence of *platinum sponge*, this change takes place in the cold and very rapidly at 100°.[35]

The vapors of *ethyl-cyclo-propane* passed at 300–310° over asbestos impregnated with anhydrous alumina, are isomerized into *methyl-ethyl-ethylene:*

$$\underset{CH_2}{\overset{CH_2}{\diagup}}\!\!\!\diagdown CH \cdot CH_2 \cdot CH_3 \;\rightarrow\; CH_3 \cdot CH : CH \cdot CH_2 \cdot CH_3.\,[36]$$
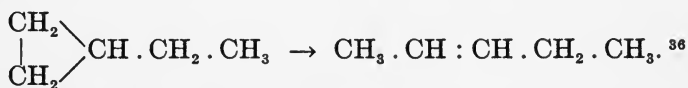
Methylene-cyclo-propane, $\underset{CH_2}{\overset{CH_2}{\diagup}}\!\!\!\diagdown C : CH_2$, passed over alumina at 350°, gives *divinyl*, $CH_2 : CH \cdot CH : CH_2$.[37]

[31] FAWORSKII, *J. Russian Phys. Chem. Soc.*, 19, 414 and 553 (1887); 20, 518 (1888), *C.*, 1887, 153.

[32] FAWORSKY, *J. prakt. Chem.*, (2), 37, 387 (1888). BÉHAL, *Bull. Soc. Chim.*, 50, 629 (1888).

[33] MERESHKOVSKI, *J. Russian Phys. Chem. Soc.*, 45, 1969 (1914), *C. A.*, 8, 1420.

[34] FAWORSKY, *J. prakt. Chem.* (2), 37, 392 (1888).

[35] TANATAR, *Zeit. phys. Chem.*, 41, 735 (1902).

[36] ROZANOV, *J. Russian Phys. Chem. Soc.*, 48, 168 (1916), *C. A.*, 11, 454.

[37] MARESHKOVSKI, *Ibid.*, 45, 2072 (1914), *C. A.*, 9, 799.

194. Cyclizations and Transformations of Ring Compounds.
Hydrobenzamide when boiled with potash changes to *amarine:* [38]

$$C_6H_5 . CH : N\diagdown \atop C_6H_5 . CH : N\diagup CH . C_6H_5 \rightarrow \quad C_6H_5 . C . NH\diagdown \atop C_6H_5 . C . NH\diagup CH . C_6H_5.$$
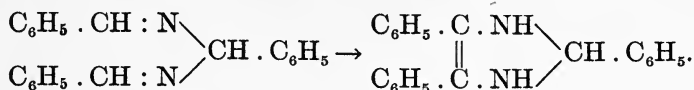
195. The *acetylenic pinacones* when kept on the water bath with a 4% water solution of mercuric sulphate, are rapidly and completely isomerized into *ketohydrofurfuranes*. Doubtless there is at first addition of water to the triple bond and then dehydration of the glycol thus obtained: [39]

$$CH_3\diagdown \atop CH_3\diagup C(OH) \cdot C : C \cdot C(OH)\diagup CH_3 \atop \diagdown CH_3 \rightarrow (CH_3)_2 : C \overset{CO - CH_2}{\underset{\diagdown O \diagup}{| \quad |}} C : (CH_3)_2$$
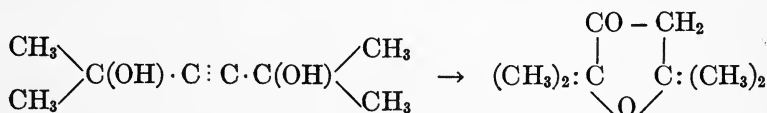
196. In contact with maleïc acid or with other acids, *dimethyl-ketazine* isomerizes into *trimethyl-pyrazoline:* [40]

$$CH_3\diagdown \atop CH_3\diagup C : N \cdot N : C\diagup CH_3 \atop \diagdown CH_2 \rightarrow \quad CH_3 \cdot CH \cdot CH_2\diagdown \atop N—NH\diagup C\diagup CH_3 \atop \diagdown CH_3$$
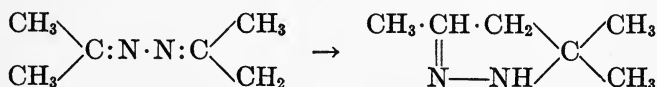
197. *Cyclo-heptane,* heated to 210° with reduced nickel in an atmosphere of hydrogen, is transformed into *methyl-cyclo-hexane,* and likewise *cyclo-octane* gives *dimethyl-cyclo-hexane.*[41]

198. *Sulphuric acid* provokes many isomerizations among the terpenes. Thus *pinene,* warmed with sulphuric acid diluted with its own volume of water, is changed to a mixture of *terpinolene, terpinene,* and *dipentene.*[42]

l.Pinene dissolved in glacial acetic acid and warmed to 60–70°, isomerizes into *l.limonene* with evolution of heat, when 5% of phosphoric acid is added.[43] Likewise *phellandrene,* on contact with sulphuric acid, yields *terpinene.*[44]

Thujone is isomerized to *isothujone* when it is warmed for nine hours with sulphuric acid diluted with two volumes of water.[45]

In the presence of sulphuric acid, *pseudo-ionone* passes into the cyclic α- and β-ionones. Thus α-ionone (artificial extract of

[38] FOWNES, *Annalen,* **54,** 364 (1845).
[39] DUPONT, *Compt. rend.,* **152,** 1486 (1911) and **153,** 275 (1911).
[40] CURTIUS and FOERSTERLING, *J. prakt. Chem.* (2), **51,** 394 (1895).
[41] WILLSTÄTTER and KAMETAKA, *Berichte,* **41,** 1480 (1908).
[42] ARMSTRONG and TILDEN, *Berichte,* **12,** 1754 (1879).
[43] PRINS, *Chem. Weekbl.,* **13,** 1264 (1916), *C. A.,* **11,** 586.
[44] WALLACH, *Annalen,* **239,** 35 (1887).
[45] WALLACH, *Annalen,* **286,** 101 (1877).

violets) is prepared by heating for 16 hours, 20 parts pseudo-ionone dissolved in 100 parts of water and 100 parts of glycerine with 2.5 parts sulphuric acid. Concentrated sulphuric acid gives mainly β-ionone. Phosphoric acid also may be employed.[46]

199. Migration of Atoms. Migrations of *halogen* atoms are frequently effected by anhydrous *aluminum chloride* or *bromide*. Thus propyl bromide, $CH_3 . CH_2 . CH_2Br$, boiled 5 minutes with 10% of aluminum bromide is completely transformed into isopropyl bromide, $CH_3 . CHBr . CH_3$; while 4% of the salt will effect the change in 24 hours in the cold.[47] The mechanism is apparently a separation into propylene and hydrobromic acid and a recombination of these to form isopropyl bromide.

Propyl chloride is affected in the same way.[48]

In the presence of anhydrous aluminum chloride at 110°, *acetylene tetrachloride*, $CHCl_2 . CHCl_2$, changes partly into the unsymmetrical tetrachlorethane, $CCl_3 . CH_2Cl$.[49]

By warming with 15 to 20% of aluminum chloride, α-bromnaphthalene, dissolved in 3 or 4 parts of carbon disulphide, is transformed into β-bromnaphthalene.[50]

200. *Mercuric chloride* and *zinc bromide* greatly accelerate the isomerization of *isobutyl bromide*, $(CH_3)_2CH . CH_2Br$, into *tertiary-butyl bromide*, $(CH_3)_3CBr$.[51]

Ethylene oxides of the type, $\begin{matrix} R \\ R' \end{matrix} \!\! > \!\! C \!\!-\!\! CH_2$, kept in contact with $\overset{\diagdown}{\underset{\diagup}{O}}$

zinc chloride, are isomerized into aldehydes, $\begin{matrix} R \\ R' \end{matrix} \!\! > \!\! CH . CHO$. Thus

ethylene oxide gives acetaldehyde.[52] The same transformation is accomplished by *anhydrous alumina* acting on the vapor of ethylene oxide at 200°.[53]

201. Concentrated or dilute *mineral acids* frequently cause the migration of atoms in a straight chain of cyclic hydrocarbon or in a ring containing nitrogen.

[46] TIEMANN and KRÜGER, *Berichte*, **26**, 2693 (1893) and 31, 808 (1898).

[47] KEKULÉ and SCHROTTER, *Berichte*, **12**, 2279 (1879). GUSTAVSON, *J. Russian Phys. Chem. Soc.*, **15**, 61 (1883).

[48] MOUNEYRAT, *Bull. Soc. Chim.* (3), **21**, 616 (1899).

[49] MOUNEYRAT, *Ibid.* (3), **19**, 499 (1898).

[50] ROUX, *Ann. Chim. Phys.* (6), **12**, 344 (1887).

[51] MICHAEL, SCHARF, and VOIGT, *J. Am. Chem. Soc.*, **38**, 653 (1916).

[52] KASCHIRSKI, *J. Russian Phys. Chem. Soc.*, **13**, 76 (1881), *C.*, **1881**, 278. KRASSUSKI, *Ibid.*, **34**, 543 (1902), *C.*, **1902**, (2), 1095.

[53] IPATIEF and LEONTOWITCH, *Beritche*, **36**, 2016 (1903).

The **1,2** *dihydrotetrazines* isomerize into the **1,4**, when heated with alcoholic hydrochloric acid,[54] thus:

$$C_6H_5 . C\underset{\diagdown NH-N-C_6H_5}{\overset{\diagup N-N\diagdown}{}}C . C_6H_5 \rightarrow C_6H_5 . C\underset{\diagdown N-N-C_6H_4}{\overset{\diagup NH-N\diagdown}{}}C \cdot C_6H_5$$
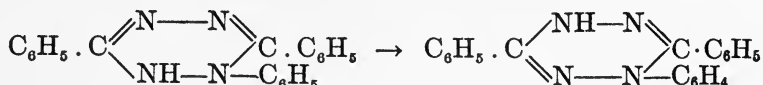
202. *Acetylchloraminobenzene*, $CH_3 . CO . NCl . C_6H_5$, is transformed into *p.chloracetanilide*, $CH_3 . CO . NH . C_6H_4Cl$, under the influence of hydrochloric acid.[55] The same acid changes hydrazobenzene into benzidene.[56]

$$\begin{array}{cc} C_6H_5-NH & C_6H_4-NH_2 \\ | & | \\ C_6H_5-NH & C_6H_4-NH_2 \end{array} =$$

203. Acids with a *double bond in* $\beta\gamma$ *position*, and *hydroxyl* in the α, are changed by boiling with dilute hydrochloric acid into γ-keto acids. Thus *phenyl-α-hydroxycrotonic* acid, $C_6H_5 . CH : CH .- CH(OH) . COOH$, is changed into *benzoyl-propionic* acid, $C_6H_5 .- CO . CH_2 . CH_2 . COOH$. The mechanism of this reaction has been variously explained.[57]

204. The *aldoximes*, $R . CH : NOH$, of the aliphatic series are changed to *amides*, $R . CO . NH_2$, by warming with sulphuric acid. To explain this change it is sufficient to assume that there is first a dehydration of the oxime to the nitrile which is hydrated by the mineral acid in the usual way to the amide.

205. In contact with sulphuric acid, *oximes* of cyclic ketones are transformed into internal amides, or iso-oximes. Thus the *oxime* of *cyclohexanone* yields the lactam of ϵ-aminocaproic acid:

$$CH_2\underset{\diagdown CH_2 . CH_2\diagup}{\overset{\diagup CH_2 . CH_2\diagdown}{}}C:NOH \rightarrow CH_2\underset{\diagdown CH_2 . CH_2 . CO}{\overset{\diagup CH_2 . CH_2 . NH}{}}$$
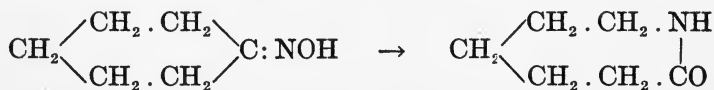
The concentrated acid, to which a little water or acetic acid has been added, is suitable for this reaction.[58]

206. *Alkaline* solutions also can cause the migration of atoms. The *potassium* salt of *diazobenzene* heated to 130° with concentrated caustic potash is changed to the *potassium* salt of *phenylnitrosamine*.[59]

[54] Stollé, *J. prakt. Chem.* (2), **73**, 299 (1906).

[55] Acree and Johnson, *Am. Chem. Jour.*, **37**, 410 (1907).

[56] Zinin, *Annalen*, **137**, 376 (1865).

[57] Fittig, *Annalen*, **299**, 20 (1898). Thiele and Sulzberger, *Ibid.*, **319**, 199 (1901). Erlenmeyer, Jr., *Ibid.*, **333**, 205 (1904). Bougault, *Ann. Chim. Phys.* (8), **15**, 513 and *Compt. rend.*, **157**, 403 (1913).

[58] Wallach, *Annalen*, **312**, 171 (1900).

[59] Schraube and Schmidt, *Berichte*, **27**, 522 (1894).

$$C_6H_5 . N : N . OK \rightarrow C_6H_5 . N \overset{\diagup NO}{\diagdown K} .$$
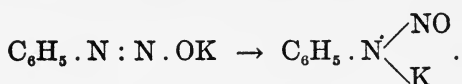
207. *Thiourea,* $CS(NH_2)_2$, on contact with a solution of *ethyl nitrite,* isomerizes into *ammonium isosulphocyanate,* $CSN . NH_4$.[60]

208. In certain cases, *finely divided metals,* copper, nickel, etc., can bring about a migration of atoms, thus causing a change of function. Thus *unsaturated alcohols* are transformed into *aldehydes* or *ketones* in a way that is easy to explain.

Allyl alcohol, $CH_2 : CH . CH_2OH$, passed in the vapor form over reduced copper at 180–300°, is changed almost entirely into *propionic aldehyde,* $CH_3 . CH_2CHO$, with only slight traces of acroleïne, $CH_2 : CH . CHO$. The hydrogen produced by the decomposition of the alcohol by the copper is immediately added to the double bond of the acroleïne.[61]

Likewise *α-unsaturated secondary alcohols,* $R . CH : CH .- CH(OH) . R'$, mixed with hydrogen over reduced nickel at 195–200°, are isomerized into the *ketones,* $R . CH_2 . CH_2 . CO . R'$.[62]

§ 2. POLYMERIZATIONS

209. Frequently several molecules of the same kind, having one or more double bonds, condense to a single molecule, which is called a *polymer* of the original molecule. The presence of a catalyst frequently causes such a change or accelerates its velocity. We will examine from this point of view:

Hydrocarbons.
Aldehydes.
Nitriles and amides.

Hydrocarbons

210. Ethylene Hydrocarbons. Hydrocarbons of the ethylene series, C_nH_{2n}, frequently change into polymers of double, triple, or even quadruple, the original molecule yet retaining the same character as the original.

Sulphuric acid, either concentrated or slightly diluted, frequently causes this polymerization. In fact, its action is complex as, besides polymerization, it can cause the addition of water to form secondary or tertiary alcohols and also the formation of acid or neutral esters

[60] CLAUS, *Annalen,* **179,** 129 (1875).
[61] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 463 (1905).
[62] DOURIS, *Compt. rend.,* **157,** 55 (1913).

of sulphuric acid. With hydrocarbons of moderate molecular weight, there is principally the formation of alcohols and esters.[63] Thus sulphuric acid diluted with its own volume of water transforms *trimethyl-ethylene*, $(CH_3)_2C : CH . CH_3$, at 0°, chiefly into *dimethyl-ethyl-carbinol*, $(CH_3)_2C(OH) . CH_2 . CH_3$.[64]

With ethylene hydrocarbons of high molecular weight, there is chiefly production of polymers, particularly *dimers*. Thus *duodecene* is changed by sulphuric acid quantitatively into viscous *tetracosene* which is stable in presence of sulphuric acid.[65]

The concentration of the acid determines the nature of the re-action. Thus α-hexene and γ-heptene, with 85% acid yield alkyl sulphuric acids, while they polymerize in contact with the normal acid, H_2SO_4.

The acid, diluted with 20% of its volume of water, changes *isobutene*, in the cold, to *tributene*, boiling at 177°.[66]

Trimethyl-ethylene in contact with sulphuric acid diluted with half its volume of water, furnishes, at 0°, much *diamylene*, boiling at 154°.[67]

211. *Zinc chloride* can polymerize unsaturated hydrocarbons, *e. g.* *trimethyl-ethylene* into *diamylene, triamylene*, and *tetra-amylene*.[68]

Boron trifluoride transforms *amylene* into *diamylene*.[69]

The use of catalysts under high pressures greatly favors the polymerization of ethylene into unsaturated hydrocarbons at high temperatures. The products obtained with *anhydrous alumina*, under 70 atmospheres above 250°, are the same as those produced by heat alone in the absence of the catalyst.[70]

Ethylene with anhydrous *zinc chloride* at 275° and 70 atmospheres, gives a gas containing 36% ethylene, 3% hydrogen, and 61% saturated hydrocarbons and a complex liquid of which 85% is *pentane* and *hexane* without any *methyl-cyclobutane*. The remainder consists of numerous hydrocarbons including unsaturated hydrocarbons boiling above 145° and *naphthenes* which are particularly abundant around 250°.

Anhydrous aluminum chloride produces little effect with ethylene at 70 atmospheres and 240°, but at 280°, a gas is obtained containing

[63] BROOKS and HUMPHREY, *J. Am. Chem. Soc.*, **40**, 822 (1918).

[64] WISCHNEGRADSKY, *Annalen*, **190**, 336 (1877).

[65] BROOKS and HUMPHREY, *Loc. cit.*

[66] BUTLEROW, *Berichte*, **6**, 561 (1873).

[67] SCHNEIDER, *Annalen*, **157**, 207 (1871).

[68] BAUER, *Jahresb.*, **1861**, 660.

[69] LANDOLPH, *Berichte*, **12**, 1578 (1879).

[70] IPATIEF, *J. Russian Phys. Chem. Soc.*, **43**, 1420 (1911), *C. A.*, **6**, 736.

only saturated hydrocarbons, and no liquid, but, instead, a rather abundant carbonaceous residue.[71]

212. Doubly Unsaturated Hydrocarbons. Acetylene is adsorbed more energetically than hydrogen by *colloidal palladium* and is to a great extent polymerized.[72]

Allylene is absorbed by concentrated *sulphuric acid* and is polymerized into *mesitylene:* [73]

$$3 \ CH_3 \ . \ C : CH = C_6H_3(CH_3)_3 (1 . 3 . 5).$$

This can be explained by assuming that the acid first causes the hydration of the allylene to acetone (308) and then dehydrates 3 molecules of this according to a well-known reaction.

Similarly *crotonylene,* or *butine*(2), shaken with slightly diluted sulphuric acid (1 part water to 3 parts acid), gives *hexamethyl-benzene.*[74]

Valerylene, C_5H_8, shaken with *sulphuric acid* changes into polymers, *trivalerylene* and *polyvalerylenes.*[75]

213. *Divinyl,* or *butadiene,* $CH_2 : CH . CH : CH_2$, as well as its higher homologs, *piperylene,* $CH_3 . CH : CH . CH : CH_2$, *isoprene,* $CH_2 : C(CH_3) . CH : CH_2$, and *dipropylene,* $CH_2 : C(CH_3) .- C(CH_3) : CH_2$, polymerize spontaneously under the influence of heat alone giving rise to various elastic solid hydrocarbons resembling natural rubber and constituting the *synthetic rubbers.* This polymerization is greatly accelerated by the presence of various catalysts. Thus with 5% metallic *sodium* or *potassium,* the reaction which goes on in the cold or with slight warming, is complete and is not hindered by the presence of non-polymerizable hydrocarbons.[76]

214. The polymerization of isoprene by *barium peroxide* or *benzoyl peroxide* or *potassium sulphide* gives rise to the intermediate formation of β-myrcene,

$$CH_2 : CH . C : CH . CH_2 . CH_2 . C : CH_2,$$
$$CH_3 \qquad\qquad CH_3$$
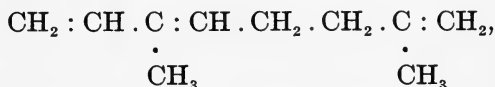
a hydrocarbon boiling at 63° at 20 mm., which, in turn, warmed with sodium or with barium peroxide changes quantitatively into *normal*

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[71] IPATIEF and RUTALA, *Berichte,* **46,** 1748 (1913).

[72] PAAL and HOHENEGGER, *Berichte,* **43,** 2684 (1910).

[73] SCHROHE, *Berichte,* **8,** 17 (1875).

[74] ALMEDINGEN, *J. Russian Phys. Chem. Soc.,* **13,** 392 (1881), *C.,* **1881,** 629.

[75] BOUCHARDAT, *Bull. Soc. Chim.* (2), **33,** 24 (1880). REBOUL, *Annalen,* **143,** 373 (1867).

[76] MATTHEWS and STRANGE, *English Pat.,* 24,790 (1910). HARRIES, *Annalen,* **383,** 157 (1911).

caoutchouc; the direct polymerization furnishes only an *abnormal caoutchouc.*[77]

215. Glacial *acetic acid* and especially *acetanhydride* acting at 150° have been recommended for the polymerization into caoutchouc,[78] the presence of 0.2% of *sulphur* or of 0.002% of *sulphuric acid* in the hydrocarbon being favorable to the reaction.[79]

Trioxymethylene, at a high temperature in an autoclave, has also been proposed as a catalyst in this reaction.[80]

216. **Cyclic Hydrocarbons.** *Pinene* heated twelve hours with formic acid changes to a hydrocarbon of double the molecular weight, $C_{20}H_{32}$.[81]

Pinene is transformed into *colophene,* $C_{20}H_{32}$, by contact with concentrated *sulphuric acid, boron fluoride,* or *phosphoric anhydride.*[82]

Pinene heated to 50° with 20% of antimony chloride is changed into tetra-terebenthine, $C_{40}H_{64}$.[83] Aluminum, ferric, and zinc chlorides cause the formation of analogous products.[84]

217. **Indene.** Indene polymerizes on contact with sulphuric acid into *para-indene,* $(C_9H_8)_x$, which melts at 120°.[85]

Aldehydes

218. The tendency to polymerize is very general among aldehydes and small traces of various materials are sufficient to cause the polymerization to take place, whether the molecules thus condensed are joined by carbon to carbon or by means of the oxygen atoms.

219. **Aldolization.** The first method of condensation is called *aldolization;* one of the aldehyde groups is preserved and the other is converted into a secondary alcohol group. The name comes from *aldol,* the first example to be studied.

Acetaldehyde kept for some time in contact with a small amount of *hydrochloric acid* or of *zinc chloride* solution condenses to give *aldol,* or butanalol (1 . 3):[86]

$$CH_3 . CHO + CH_3 . CHO = \underset{\text{aldol}}{\underline{CH_3 . CH(OH) . CH_2 . CHO}}$$
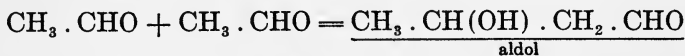
[77] OSTROMUISLENSKII and KOSHELEV, *J. Russian Phys. Chem. Soc.,* **47**, 1928 (1915), *C. A.,* **10**, 1947. OSTROMUISLENSKII, *Ibid.,* **48**, 1071 (1916), *C. A.,* **11**, 1768.

[78] CHEM. FABR. AUF. ACTIEN, *French Patent,* 433,825.

[79] BADISCHE, *French Patent,* 434,587.

[80] GROSS, *French Patent,* 459,987.

[81] LAFONT, *Ann. Chim. Phys.* (6), **15**, 179 (1888).

[82] SAINTE-CLAIRE-DEVILLE, *Ibid.* (2), **75**, 66 (1839) and (3), **26**, 85 (1849).

[83] PRINS, *Chem. Weekbl.,* **13**, 1264 (1916), *C. A.,* **11**, 586.

[84] RIBAN, *Ann. Chim. Phys.* (5), **6**, 42 (1875).

[85] KRÄMER and SPILKER, *Berichte,* **23**, 3278 (1890).

[86] WURTZ, *Compt. rend.,* **74**, 1361 (1872) and **76**, 1165 (1873).

The same result is obtained more readily by leaving acetaldehyde for 18 hours in contact with a solution of *neutral potassium carbonate* or with a fragment of solid *caustic potash*.[87] Also in the presence of *zinc turnings* at 100°, acetaldehyde gives aldol and likewise *crotonic aldehyde* by loss of water (795).

220. Likewise *benzaldehyde* heated with an alcoholic solution of *potassium cyanide* (10% of the weight of the aldehyde), is rapidly transformed into *benzoïne*, $C_6H_5 . CH(OH) . CO . C_6H_5$.[88] The original aldehyde group is in this case changed to a ketone.

Anisaldehyde, $CH_3O . C_6H_4 . CHO$, with the same reagent, gives *anisoïne*, $CH_3 . O . C_6H_4 . CH(OH) . CO . C_6H_4 . O . CH_3$.[89]

On heating an hour and a half, the same catalyst transforms *cuminaldehyde* into *cuminoïne*,[90] and in half an hour, *furfural* into *furfuroïne*.[91]

221. The aldolization of several molecules of aldehyde can be realized successively or simultaneously.

Under the influence of milk of lime, *formaldehyde* condenses to a hexose, $CH_2(OH) . CH(OH) . CH(OH) . CH(OH) . CO . CH_2OH$, which is *racemic laevulose*.[92] Analogous condensations giving inactive *arabinose* and laevulose, are realized in contact with *granulated tin*,[93] or with a mixture of *magnesia, magnesium sulphate,* and *granulated lead*.[94] A similar condensation can be obtained starting with *trioxymethylene*, $(HCOH)_3$.[95]

222. **Second Method.** The second method in which aldehydes polymerize suppresses the aldehyde function, producing bodies called *paraldehydes* and *metaldehydes,* the vaporization of which tends to reproduce the original aldehyde.

Acetaldehyde in contact with small quantities of *sulphur dioxide,* anhydrous *zinc chloride, hydrogen chloride,* or *carbonyl chloride* soon warms up and is converted into *paraldehyde,* boiling at 124°. The same result is obtained by warming it with *ethyl iodide* or by leaving a solution of *cyanogen* in acetaldehyde to stand for several days.[96]

[87] MICHAEL and KOPP, *Am. Chem. Jour.*, **5**, 190 (1883).

[88] WÖHLER and LIEBIG, *Annalen*, **3**, 276 (1832). ZININ, *Ibid.*, **34**, 186 (1840). BREUES and ZINCKE, *Ibid.*, **198**, 151 (1879).

[89] ROSSEL, *Ibid.*, **151**, 33 (1869).

[90] BÖSLER, *Berichte*, **14**, 324 (1881).

[91] E. FISCHER, *Annalen*, **211**, 218 (1882).

[92] LOEW, *Berichte*, **22**, 475 (1889). E. FISCHER and PASSMORE, *Ibid.*, **22**, 359 (1889).

[93] LOEW, *J. prakt. Chem.* (2), **34**, 51 (1886).

[94] LOEW, *Loc. cit.*

[95] SEYEWETZ and GIBELLO, *Compt. rend.*, **138**, 150 (1904).

[96] LIEBEN, *Annalen, Supl. Band,* **1**, 114 (1861).

A few bubbles of *hydrogen chloride* or *sulphur dioxide* passed into acetaldehyde cooled below 0°, convert it into metaldehyde, a sublimable solid.[97]   By adding one drop of *concentrated sulphuric* acid to 100 cc. acetaldehyde, *paraldehyde* is obtained.

223. Likewise by passing a few bubbles of *hydrogen chloride* into *propionic aldehyde* cooled below 0°, crystals of *metapropanal* (melting at 180°) are obtained along with *parapropanal,* a liquid boiling at 169°. By a current of hydrogen chloride at —20°, *metapropanal* is formed.[98]

When a current of dry hydrogen chloride is passed into *butanal* at —20°, heat is evolved and, on stopping the gas, crystals of *metabutanal* (melting at 173°) separate out along with oily *parabutanal.*

Under the same conditions, *cenanthal* (heptaldehyde) gives *paraheptaldehyde* (melting at 20°) and *metaheptaldehyde* (melting at 140°).[99]

224. *Isobutyric aldehyde,* with a concentrated solution of sodium acetate at 150°, is changed into the *dialdehyde* boiling at 136°.[100] With a little chlorine, bromine, iodine, hydrochloric acid, phosphorus pentachloride or zinc chloride, *meta-isobutanal,* melting at 59°,[101] is produced.

With alcoholic potash it gives in succession, *tri-isobutanal* (b.154°), *tetra-isobutanal* (b.190°), *penta-isobutanal* (b.223°), *hexa-isobutanal* (b.250°), and finally oily *hepta-isobutanal.*[102]

Chloral behaves similarly in contact with various substances, forming solid insoluble *metachloral* with *sulphur dioxide. Trimethyl amine* produces the same effect rapidly;[103] *fuming sulphuric acid* causes the same polymerization,[104] while *pyridine* gives *metachloral* in a gelatinous form.[105]

225. **Third Method.** Aromatic aldehydes, *e. g. benzaldehyde,* when warmed with alkali, undergo a special change, yielding the alcohol and acid at the same time:

$$2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CO_2K + C_6H_5 \cdot CH_2OH \cdot$$

[97] KEKULÉ and ZINCKE, *Ibid.,* **162,** 125 (1872).

[98] ORNDORF, *Amer. Chem. J.,* **12,** 353 (1890).

[99] FRANKE and WOZELKA, *Monatsh.,* **33,** 349 (1912).

[100] FOSSEK, *Ibid.,* **2,** 622 (1881).

[101] BARBAGLIA, *Berichte,* **5,** 1052 (1872) and **6,** 1064 (1873). DEMTSCHENKO, *Ibid.,* **6,** 1176 (1873).

[102] PERKIN, *J. Chem. Soc.,* **43,** 91 (1883).

[103] MEYER and DULK, *Annalen,* **171,** 76 (1874).

[104] BÖESEKEN, *Rec. Trav. Chim. Pays-Bas,* **29,** 104 (1910).

[105] BÖESEKEN and SCHIMMEL, *Ibid.,* **32,** 112 (1913).

Formaldehyde gives the same reaction to some extent with dilute *caustic soda.*[106] On the contrary, *acetaldehyde,* with caustic soda or potash, polymerizes into a complex resin.

226. *Isobutyric aldehyde* with *baryta water* reacts somewhat like aromatic aldehydes, yielding *isobutyl isobutyrate:*

$$(CH_3)_2CH \cdot CHO + CHO \cdot CH(CH_3)_2 = (CH_3)_2CH \cdot CO \cdot OCH_2 \cdot CH(CH_3)_2 \cdot$$
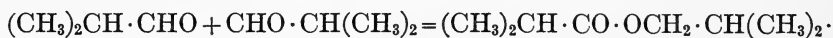
When the solution is warmed, the ester is saponified into *isobutyl alcohol* and *isobutyric acid.*[107]

227. This reaction takes place with all *aliphatic aldehydes* in which the carbon atom next to the aldehyde group carries no hydrogen.

It is sometimes caused by the presence of *ethyl magnesium iodide.* With 2,2-*dimethyl-propanolal* the *hydroxypivalic* ester of 2,2-*dimethyl-propandiol* is obtained: [108]
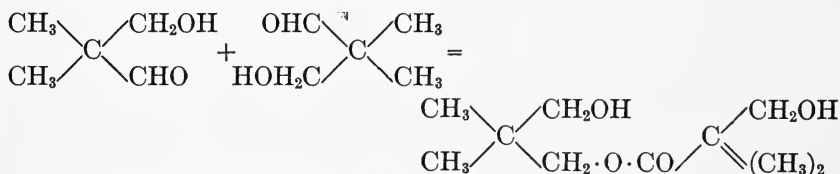
228. The same reaction can be brought about with the lower aliphatic aldehydes by the use of *aluminum ethylate,* $Al(OC_2H_5)_3$ (299). Thus *formaldehyde* is condensed into *methyl formate, acetaldehyde* into *ethyl acetate,* *propionic aldehyde* into *propyl propionate,* even *chloral* into *trichlorethyl trichloracetate.*[109]

In the case of acetaldehyde this reaction goes quantitatively in 24 hours if 4% of ethyl aluminate be used and the mixture kept below 15°. The ethylate can be used in solution in ethyl acetate, xylene,[110] or *solvent naphtha.*[111]

The reaction is carried out in this way: To 135 parts of acetaldehyde, 6 parts of aluminum ethylate containing 10% aluminum chloride are added little by little and the mixture let stand for ten hours. The yield is 123 parts ethyl acetate.[112]

[106] H. & A. EULER, *Berichte,* **38**, 2556 (1905).

[107] FRANKE, *Monatsh. Chem.,* **21**, 1122 (1900).

[108] FRANKE and KOHN, *Ibid.,* **25**, 865 (1904).

[109] TISCHENKO, *J. Russian Phys. Chem. Soc.,* **33**, 260 (1901).

[110] KONSORTIUM F. ELEKTROCH. IND., *English pat.,* 26,825 and 26,826 of 1913. *J. S. C. I.,* **33**, 666 (1914). *German pat.,* 277,188 (1913); IMRAY, *English pat.,* 1,288 of 1915, *J. S. C. I.,* **35**, 141 (1916).

[111] *German pat.,* 308,043 (1918), *Chem. Centr.,* **1918** (2), 613.

[112] KONSORTIUM F. ELEKTROCH. IND., *French patent,* 465,965. *J. Soc. Chem. Ind.,* **33**, 666 (1914).

Ketones

229. The ketones rarely polymerize but usually condense with the loss of water.

However, aldolization of acetone takes place in the cold with a concentrated solution of caustic soda.[113]   Thus:

$$CH_3 \cdot CO \cdot CH_3 + CO \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix} = CH_3 \cdot CO \cdot CH_2 \cdot C(OH) \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$$
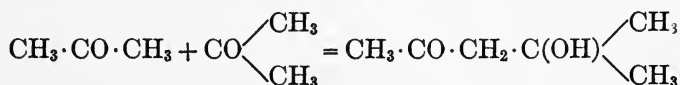
When the product is heated with the same alkali, the reaction is reversed.

Nitriles and Amides

230. *Hydrocyanic acid,* or *formic nitrile,* HCN, kept with *caustic potash* or an alkaline carbonate, desposits crystals of the empirical formula $(CNH)_3$ which are soluble in ether and appear to be the *nitrile* of *amino-malonic* acid, $CN \cdot CH(NH_2) \cdot CN$, along with brown amorphous material.[114]   The same substance is obtained when a small fragment of solid *potassium cyanide* is added to a water solution of hydrocyanic acid.[115]

231. *Propionic nitrile,* $CH_3 \cdot CH_2 \cdot CN$, dissolved in its own weight of anhydrous ether in contact with 20% metallic *sodium* is converted into *dipropionic nitrile,* melting at 47°.[116]   Under the same conditions, *acetonitrile,* $CH_3 \cdot CN$, is converted into *diacetonitrile,* $CH_3 \cdot C(NH) \cdot CH_2 \cdot CN$, melting at 52°.[117]

232. When the same nitriles, pure and without the ether, are heated with metallic *sodium* or *potassium* (1 of metal to 9 of nitrile), they are polymerized into their trimers, *acetonitrile* into *cyanethine,* $(C_2NH_3)_3$.[118]

Benzonitrile polymerizes on contact with sulphuric acid into *cyaphenine:* [119]
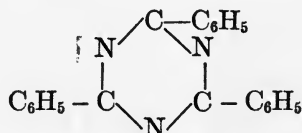
[113] KOELICHEN, *Z. phys. Chem.,* **33**, 129 (1900).

[114] WIPPERMANN, *Berichte,* **7**, 767 (1874).

[115] LESCOEUR and RIGAUT, *Compt. rend.,* **89**, 310; *Bull. Soc. Chim.* (2), **34**, 473 (1880).

[116] VON MEYER, *J. prakt. Chem.* (2), **38**, 337 (1888).

[117] HOLTZWART, *Ibid.* (2), **39**, 230 (1889).

[118] FRANKLAND and KOLBE, *Annalen,* **65**, 269 (1848). BAYER, *Berichte,* **2**, 319 (1869) and **4**, 176 (1871). VON MEYER, *J. prakt. Chem.* (2), **27**, 153 (1883).

[119] HOFMANN, *Berichte,* **1**, 198 (1868).

233. *Cyanamide,* either in the cold in contact with concentrated caustic *soda* or *potash,* or in a hot solution to which is added a little ammonia, is transformed into *dicyanamide.*[120]

§ 3. DEPOLYMERIZATIONS

234. Depolymerizations are far more rare than polymerizations, since the polymers usually correspond to a much more stable molecular state. In exceptional cases, polymers can be decomposed into the simple molecules by the action of heat and this return is greatly facilitated by the very catalysts that cause the polymerization.

This is the case with *paraldehydes* and *metaldehydes.* The catalysts which at low temperature polymerize the aldehydes into their trimers break these up at high temperatures to regenerate the aldehydes. A trace of concentrated *sulphuric acid, hydrochloric acid, calcium* or *zinc chloride* or the like is sufficient to change hot *paraldehydes* into the monomolecular aldehydes.[121] Likewise *metaldehydes* are transformed into the aldehydes by heating with dilute sulphuric acid.[122]

Certain aldols can be decomposed, by warming with a trace of potassium carbonate, regenerating the two molecules of the original aldehyde. But with benzoïne and analogous compounds this decomposition does not take place simply.

235. The transformation of *pinene* and especially of *dipentene,* $C_{10}H_{16}$, into *isoprene,* C_5H_8, which is realized by the action of an incandescent platinum spiral,[123] appears to be due to the catalytic action of the metal, for this reaction can be caused by passing the vapors of the terpene over pumice impregnated with platinum black in an iron tube at a very low red.[124]

§ 4. CONDENSATIONS BETWEEN DISSIMILAR MOLECULES

Aldehydes and Ketones

236. *Aldehydes* and *ketones* can add molecules of other kinds, the reactions being comparable to aldolizations and aided by catalysts of the same nature.

[120] HAAG, *Annalen,* **122**, 22 (1862). BAUMANN, *Berichte,* **6**, 1373 (1873). GRUBE and KRÜGER. *Zeit. phys. Chem.,* **86**, 65 (1914).

[121] FRANKE and KOHN, *Monatsh. Chem.,* **19**, 354 (1898).

[122] BURSTYN, *Ibid.,* **23**, 737 (1902).

[123] HARRIES and GOTTLOB, *Annalen,* **383**, 228 (1911). STAUDINGER and KLEVER, *Berichte,* **44**, 2212 (1911).

[124] SCHORGER and SAYRE, *J. Ind. Eng. Chem.,* **7**, 924 (1915).

This reaction is general between *aldehydes* and *nitroparaffines* and gives *nitroalcohols*. The presence of an alkali, or better an *alkali carbonate,* is sufficient to cause the reaction.

By adding a small fragment of *potassium bicarbonate* to a mixture of equal molecules of *nitromethane* and *acetaldehyde,* with an equal volume of water, 1–*nitropropanol*(2) is obtained: [125]

$$CH_3 \cdot CO \cdot H + CH_3NO_2 = CH_3 \cdot CH(OH) \cdot CH_2NO_2 \cdot$$
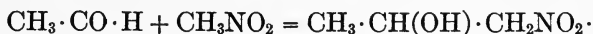
Likewise *nitroethane* condenses with formaldehyde in the presence of a little neutral *potassium carbonate* to give 2–*nitropropyl alcohol,* $CH_3 \cdot CH(NO_2) \cdot CH_2OH$.[126]

Several aldehyde molecules may take part in the reaction. *Nitropropane* and formaldehyde with a little potassium carbonate give 2–*nitro-methanol*(2)–*butanol*(1): [127]

$$CH_3 \cdot CH_2 \cdot CH_2NO_2 + 2HCHO = CH_3 \cdot CH_2C(NO_2)(CH_2OH)_2 \cdot$$
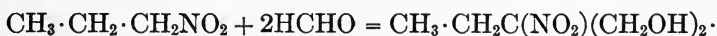
A mixture of *formaldehyde* (commercial formaldehyde solution) and *nitro-methane* reacts violently on the addition of a fragment of potassium bicarbonate to give 2–*nitro-methylol*(2)*propanediol*(1,3), a nitro-triprimary alcohol melting at 158°.[128]

$$3HCHO + CH_3NO_2 = C(NO_2)(CH_2OH)_3 \cdot$$
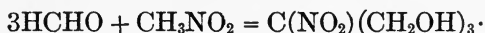
237. The mixture of *glyceric aldehyde* and *dihydroxyacetone* which is produced by the air-oxidation of glycerine in the presence of finely divided platinum (92), condenses into *i-laevulose* in contact with a water solution of *caustic soda:* [129]

$$CH_2OH \cdot CHOH \cdot CHO + CH_2OH \cdot CO \cdot CH_2OH =$$
$$CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CO \cdot CH_2OH \cdot$$
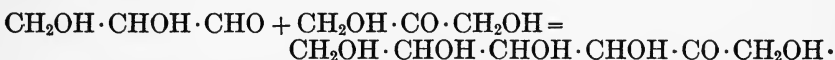
238. *Acetone* reacts with *chloroform* in the presence of solid *caustic potash* to give *acetone-chloroform* or *trichlor-tertiary-butyl alcohol:*

$$(CH_3)_2CO + HCCl_3 = (CH_3)_2 \cdot C(OH) \cdot CCl_3 \cdot$$
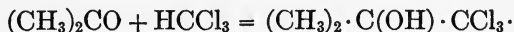
To a mixture of 500 parts acetone and 100 parts chloroform, 300 parts of pulverized caustic potash are added very slowly and the mixture left for 36 hours.[130]

239. *Anhydrous aluminum chloride* can sometimes cause the same

[125] HENRY, *Bull. Soc. Chim.* (3), 13, 993 (1895).

[126] HENRY, *Ibid.,* 15, 1223 (1896).

[127] PAUWELS, *Chem. Centbl.,* 1898 (1), 193.

[128] HENRY, *Compt. rend.,* 121, 210 (1895).

[129] E. FISCHER and TAFEL, *Berichte,* 22, 106 (1882). WOHL and NEUBERG, *Ibid.,* 33, 3098 (1900).

[130] WILLGERODT and GENIESER, *J. prakt. Chem.* (2), 37, 361 (1888).

sort of reactions Thus *chloral* gives an addition compound with naphthalene, $C_{10}H_7 . CH(OH) . CCl_3$.[131]

240. *Acetylation of Aldehydes.* The addition of the *anhydrides* of monobasic organic acids to aldehydes yields esters of the ethylidene glycols corresponding to the aldehydes. This reaction is catalyzed by the presence of various metal salts, *copper sulphate, zinc chloride, ferric chloride,* and *stannic chloride* and even by sulphuric acid. Thus *benzaldehyde* and *acetanhydride* give *benzylidene acetate* quantitatively in the presence of copper sulphate:

$$C_6H_5 \cdot CHO + (CH_3CO)_2O = C_6H_5 \cdot CH(O \cdot COCH_3)_2 \cdot$$
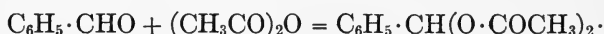
In the presence of stannic chloride, *vanilline* gives a quantitative yield of the *triacetate,* the phenol group being simultaneously acetylated.[132]

Hydrocarbons

241. Unsaturated hydrocarbons, *ethylenic* or *acetylenic,* may add themselves to hydrocarbons in the presence of aluminum chloride.[133] By passing *acetylene* into *benzene* containing aluminum chloride, symmetrical *diphenyl-ethane* is obtained: [134]

$$C_6H_6 + CH \vdots CH + C_6H_3 = C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$$

and also a certain amount of *styrene* formed by the addition of only one molecule of benzene:

$$C_6H_6 + CH \vdots CH = C_6H_5 \cdot CH : CH_2.$$
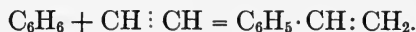
By passing *ethylene* into a warm mixture of *diphenyl* and aluminum chloride, *ethyl-diphenyl* is obtained:

$$C_6H_5 \cdot C_6H_5 + CH_2 : CH_2 = C_6H_5 \cdot C_6H_4 \cdot CH_2 \cdot CH_3$$
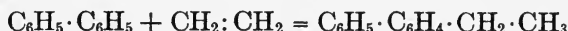
along with some of the *diethyl* derivative.[135]

242. In an analogous way anhydrous aluminum chloride causes the addition of carbon tetrachloride or of chloroform to *ethylenic chlorine derivatives.*

Thus *trichlorethylene,* $CCl_2 : CHCl$, gives, with carbon tetra-

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[131] Frankforter and Daniels, *J. Amer. Chem. Soc.,* **37,** 2560 (1915).

[132] Knoevenagel, *Annalen,* **402,** 111 (1913).

[133] This may be considered as a case of the Friedel and Crafts reaction. A trace of water is always present and reacts with the aluminum chloride to give hydrochloric acid which adds to the hydrocarbon to form an alkyl chloride which then reacts in the usual way liberating hydrochloric acid which repeats the reaction. — E. E. R.

[134] Varet and Vienne, *Bull. Soc. Chim.* (2), **47,** 919 (1887).

[135] Adam, *Bull. Soc. Chim.* (2), **47,** 689 (1887) and *Ann. Chim. Phys.* (6), **15,** 252 (1888).

chloride, *heptachlorpropane*, $CCl_3 . CHCl . CCl_3$, boiling at 249°, and with chloroform, *hexachlorpropane*, $CCl_3 . CHCl . CHCl_2$, boiling at 216°.

Likewise *dichlorethylene*, $CHCl : CHCl$, and chloroform give symmetrical *pentachlorpropane*, $CHCl_2 . CHCl . CHCl_2$, boiling at 198°.[136] See Chapter XX for the reverse reactions caused by aluminum chloride.

243. *Stannic chloride* causes an analogous addition of *ethylenic* or *cyclohexenic* chlorides to *acid chlorides* to form α-*chlorketones*. Aluminum chloride also can be used as catalyst in the reaction but is not so good.[137]

[136] PRINS, *J. prakt. Chem.* (2), **89**, 414 (1914).
[137] DARZENS, *Compt. rend.*, **150**, 707 (1910).

CHAPTER V

OXIDATIONS

I. Direct Oxidations by Gaseous Oxygen

244. The action of oxygen on various substances, or *oxidations*, can be divided into three groups:

1. Oxidations which take place spontaneously as soon as the oxidisable material and oxygen are brought together under the proper conditions of temperature and pressure.[1]

2. Oxidations which are brought about by the simultaneous oxidation of certain substances called *auto-oxidisers*.

3. Oxidations effected by substances which are apparently unchanged and which are called *oxidation catalysts*.

At first sight only the latter seem to belong in the present treatise. But even in the first group, catalytic phenomena are of more or less importance. We have already mentioned (73) the influence of moisture on reactions. Practically, the amounts of water vapor contained in the air or in the oxygen, even when they are dried by the usual means, are sufficient to facilitate oxidations of the first class.

The case of induced oxidations, that is as a consequence of simultaneous oxidations, has been examined in Chapter III (150), and we have shown how we can sometimes pass from the mechanism of such reactions to catalytic oxidations which should be specially examined.

245. **Platinum.** The direct formation of a sort of unstable oxide on the surface of the platinum (154) permits us to explain the important rôle of this metal in many oxidations. Its activity should be proportional to its surface and it can be shown that the surface is immeasurably larger for *platinum sponge* and especially for the *black* than it is for the same amount of metal in foil or wire.

246. The use of platinum black enables us to effect many oxidations. Ethyl alcohol poured on platinum black is vigorously oxidised to acetaldehyde and acetic acid; the black is sometimes made incandescent and the alcohol may take fire.

[1] In cases of this kind it is practically impossible to eliminate the catalytic effect of the interior surfaces of the walls of the containing vessel and hence it is sometimes difficult to distinguish between reactions of this kind and those of Class 3. — H. D. Gibbs.

Formic and *oxalic acids* are burned to water and carbon dioxide.[2]

Alcohols are usually oxidised to aldehydes and even to acids. Cinnamic aldehyde can be obtained thus from the corresponding alcohol.[3]

By oxidising glycerine by air in the presence of platinum black, the isomers, glyceric aldehyde and dihydroxyacetone, are obtained:[4]

$$CH_2OH \cdot CHOH \cdot CH_2OH + O = H_2O + CH_2OH \cdot CHOH \cdot CHO$$
$$CH_2OH \cdot CHOH \cdot CH_2OH + O = H_2O + CH_2OH \cdot CO \cdot CH_2OH \cdot$$
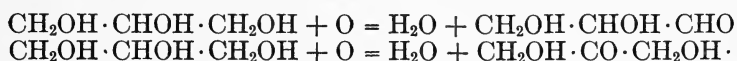
However, platinum black has no effect on a mixture of carbon monoxide and oxygen.[5]

247. The results given by the black are irregular because its action is too violent, particularly at the beginning of the reaction.

By substituting for it, platinized asbestos where the active material is diluted by a large proportion of inert material, regular oxidation of vapors mixed with suitable amounts of oxygen or of air, is obtained. The manufacture of sulphur trioxide is only an application of this on the large scale.

248. *Colloidal platinum* (67) has intense oxidising power, greater than that of the black. It gives 50% carbon dioxide with a mixture of *carbon monoxide* and half its volume of oxygen.[5]

249. Platinum in very fine wire or very thin foil is employed industrially in the oxidation of *ammonia gas* by the oxygen of the air. The gaseous mixture, previously heated to about 300°, is passed over the metal which is thereby maintained in incandescence.[6] Contact with the metal for one-five-hundredth of a second is sufficient to obtain a good yield of nitrous vapors which are easily transformed into nitric acid.

It furnishes also an excellent method for the regular oxidation of alcohols and of other sufficiently volatile organic substances.[7] Trillat has described a method of operating which makes it easy to attain this end by the aid of a platinum wire which is heated by a current that can be regulated at will for any desired temperature [8] and over which a current of air passes laden with the vapors of the substance to be oxidised.

[2] Mulder, *Rec. Trav. Chim. Pays-Bas*, **2**, 44 (1883).

[3] Strecker, *Annalen*, **93**, 370 (1855).

[4] Grimaux, *Bull. Soc. Chim.* (2), **45**, 481 (1886).

[5] Paal, *Berichte*, **49** 548 (1916).

[6] The points that are used in pyrography for burning designs on wood contain leaves of platinum foil which are heated by the catalytic combustion of the mixture of air and combustible vapors forced over them. — E. E. R.

[7] Better catalysts than platinum are known for the oxidation of many alcohols. See note to 254 *infra.* — H. D. Gibbs.

[8] Trillat, *Bull. Soc. Chim.* (3), **27**, 797 (1902).

Under these conditions methyl alcohol is oxidised below 200° chiefly to formaldehyde with some methylal and water but no acid. The acid appears when the spiral reaches a dull red, at the same time that the formaldehyde and methylal increase. At a cherry red these decrease and the proportion of carbon dioxide increases with increase of incandescence.

The presence of water in the methyl alcohol favors the oxidation which goes best when 20% of water is present.

Ethyl alcohol is oxidised as low as 225° and readily at a dull red with a yield of 16.8% of acetaldehyde and 2.3% acetal. The results are less and less favorable as the molecular weight of the alcohol increases.

With *propyl alcohol* the yield of aldehyde is about the same as with ethyl, but is 12% for normal *butyl alcohol* and 5% for *isobutyl*. *Isopropyl alcohol* gives 16% acetone. *Tertiary butyl alcohol* breaks up, on oxidation, into formaldehyde, acetone and water.

Allyl alcohol gives 5.8% acroleïne, some acrylic acid, formaldehyde and glyoxal.

Glycol oxidises at 90°, raising the spiral to incandescence and yielding *formaldehyde, glycolic aldehyde* and *glyoxal*.[9] Glycerine gives principally formaldehyde and acroleïne.

Aromatic alcohols likewise produce some of the corresponding aldehyde. *Benzyl alcohol* has furnished 4% *benzaldehyde* and *cuminyl alcohol*, 5.7% cuminic aldehyde.

Cinnamic alcohol gives some cinnamic aldehyde at a dull red and cinnamic acid and benzaldehyde at higher temperatures.

Isoeugenol oxidises at a dull red to give 2.9% vanilline mixed with the unchanged substance.[10]

250. The use of porous porcelain impregnated with platinum is advantageous for securing the complete oxidation of organic compounds in combustion analysis.[11]

251. Metals of the Platinum Group. The various metals of this family may be used as sponge or better as black for the same purposes.

Palladium black gives good results.[12]

Osmium, a more moderate catalyst, sometimes has advantages. In the oxidation of cyclohexene, it gives some cyclohexenol accom-

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[9] Trillat, *Bull. Soc. Chim.* (3), **29**, 35 (1903).

[10] Trillat, *Bull. Soc. Chim.* (3), **29**. 35 (1903).

[11] Carrasco and Belloni, *J. Pharm. and Chim.* (6), 27, 469; *Chem. Centbl.,* 1908 (2), 95.

[12] Wieland, *Berichte,* **46**, 3327 (1913).

panied by adipic acid and other products. The other metals of the *platinum* family are not suitable for these reactions.

Tellurium may be used, but it is less active than osmium.[13]

Colloidal irridium can catalyze the oxidation of carbon monoxide as does colloidal platinum, but *colloidal osmium* is less efficient.[14]

252. Gold and Silver. Gold and silver can be substituted for platinum in the preparation of *formaldehyde*. Silvered asbestos obtained by the reduction of the nitrate by formic acid and asbestos gilded by the reduction of the chloride are more active than platinized asbestos (245).[15]

253. Copper. In the oxidation of methyl alcohol by the method of Trillat (248), the platinum spiral can be replaced by a roll of copper gauze heated to a dull red.

The results obtained are entirely similar. In operating thus with a current of 2.3 to 2.7 liters of air per minute, carrying 0.5 to 0.8 g. methyl alcohol, copper gauze gives a yield of 48.5% formaldehyde at 330°. There is at the same time production of carbon monoxide, carbon dioxide and water vapor.[16]

The direct oxidation of methane by air in contact with copper or silver is a practicable method for preparing formaldehyde. A mixture of one volume of moist air with three volumes of methane is passed over either of these metals or over a mixture of the two. The formaldehyde that is produced is taken out by contact with water and the residual gases are passed again over the catalyst.[17]

254. Fokin, operating under identical conditions with air saturated with methyl alcohol vapor passed over various catalysts, has obtained the following yields of formaldehyde (figured on the methyl alcohol used): [18]

Gilded asbestos	71%
Silvered asbestos	64–66
Coppered asbestos	43–47
Platinized asbestos	5.2
Reduced cobalt	2.8
Manganese in powder	2
Aluminum turnings	1.5
Reduced nickel	1.08

[13] WILLSTÄTTER and SONNENFELD, *Berichte*, **46**, 2952 (1913).

[14] PAAL, *Berichte*, **49**, 548 (1916).

[15] FOKIN, *J. Russian Phys. Chem. Soc.*, **45**, 286 (1913); *C. A.*, **7**, 2227.

[16] ORLOFF, *J. Russian Phys. Chem. Soc.*, **39**, 855 and 1023 (1907); *C. A.*, **2**, 263 and 1692.

[17] VEREIN F. CHEM. IND., *German patent*, 286,731, *J. Soc. Chem. Ind.*, **35**, 73 (1916).

[18] FOKIN, *J. Russian Phys. Chem. Soc.*, **45**, 286 (1913); *C. A.*, **7**, 2227.

A maximum yield of 84% was obtained by a mixture of silver and copper. The silvered or gilded asbestos requires an initial temperature of only 200–250° and the heat evolved is sufficient to maintain it at a suitable temperature.

Copper used alone requires continual heating, but this can be avoided by placing ahead of the copper gauze some fragments of pumice impregnated with platinum or palladium the incandescence of which heats the gas sufficiently.[19]

The presence of lead in the copper is unfavorable.

Ethyl, propyl, isobutyl and isoamyl alcohols may be oxidised under like conditions.[20] Ether is oxidised to formaldehyde and acetaldehyde.[21] Various hydrocarbons have been submitted to regular oxidation by the same process but the products have not been fully studied.[22]

255. As acetaldehyde can be prepared from acetylene (309), its direct oxidation to acetic acid is an interesting industrial problem.

It appears to be realized by the use of platinum; the aldehyde vapors carried by air or oxygen over platinized asbestos kept at 130-40° are regularly transformed into acetic acid.[23]

256. The same metals may be used as catalysts for the direct oxidation of ammonia or amines.

Moist *ammonia* yields ammonium nitrite with a little nitrate and very little free nitrogen.

Moist *methyl amine* gives formaldehyde along with ammonium nitrite and nitrate, while ethyl amine gives some acetaldehyde.

Dimethylaniline produces formaldehyde and a complex aromatic amine.[24] Aniline, toluidine and pyridine are oxidised with the formation of complex oily products.[25]

[19] The oxidation of isopropyl alcohol has been extensively investigated by R. R. Williams and H. D. Gibbs in connection with the utilization of the waste unsaturated gases obtained in large quantities from the petroleum cracking stills. It was found that the best catalyst was brass (zinc and copper). The isopropyl alcohol is mixed with air and passed through brass gauze at about 200°. With a catalytic chamber of a proper volume in relation to the radiation surface, the reaction is continuous and requires no external heat. The yield of acetone is over 90% of the theory. That the reaction is essentially a dehydrogenation is shown by passing the isopropyl alcohol over the catalyst without the oxygen of the atmosphere, acetone is formed but the necessary heat must be supplied externally. This work was done for the U. S. Government during the war but the report has not yet been published. — H. D. Gibbs.

[20] Orloff, *Ibid.*, 40, 203 (1908); *C. A.*, 2, 3346.

[21] Orloff, *Ibid.*, p. 799; *C. A.*, 3, 1147.

[22] Orloff, *Ibid.*, p. 652.

[23] Dreyfus, *French patent*, 487,412 (1918).

[24] Trillat, *Bull. Soc. Chim.* (3), 29, 873 (1903).

[25] Orloff, *J. Russian Phys. Chem. Soc.*, 40, 659 (1908).

257. Carbon. The less combustible forms of carbon may serve as oxidation catalysts.

Coke at 200° aids in transforming toluene into benzoic acid.[26][27]

Coal and *lignite* after being heated in the air to 300° are good oxidation catalysts between 150 and 300°; the action, being partly due to the oxide of iron which they contain, is increased by the addition of ferric oxide. They can be used in the oxidation of ethyl alcohol to acetaldehyde and acetic acid, and of toluene into benzaldehyde and benzoic acid. Anthracene gives anthraquinone and borneol forms camphor and camphoric acid.[28]

258. Metallic Oxides. A large number of metallic oxides act as oxidation catalysts and for the most of them this property can be readily explained by the fact that they are readily reduced to the metals or to lower oxides by the substances to be oxidised and are readily reoxidised directly by oxygen. This is the case with the oxides of copper, nickel and cobalt. When alcohol vapors alone are passed over copper oxide moderately heated, aldehyde is formed and the oxide is reduced, but if the air is mixed with the alcohol vapors the copper is immediately reoxidised and can recommence the oxidation of the alcohol. A like explanation fits the case of *ferric oxide*, which can be reduced to a lower oxide which is reoxidised by the air. It is more difficult to perceive the mechanism in the case of oxides which can not be reduced to suboxides *e. g. chromium sesquioxide* which is, nevertheless, an excellent oxidation catalyst.[29]

The catalytic activity of *iron sesquioxide*, such as is obtained by roasting pyrites, is utilized industrially in the manufacture of sulphuric acid by the contact process.

259. The use of metallic oxides as catalysts in the oxidation of organic compounds has until recent years been limited to *copper oxide*

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[26] DENNSTEDT and HASSLER, *German patent,* 203,848, *Chem. Centrbl.,* **1908,** (2), 1750.

[27] During the war various forms of carbon were extensively studied as adsorbents for gases and as catalysts for certain reactions. Very active forms of charcoal were developed by high heat treatments. These charcoals were found to be excellent clarifying agents for solutions, and some forms catalyzed certain reactions to a high degree. The reaction between chlorine and water was found to be quite rapid at low temperatures, even so low as 0°, and at 100° it is very vigorous. The reaction is $2 Cl_2 + 2H_2O \rightarrow 4 HCl + O_2$. This would constitute a reversal of the Deacon process were it not for the fact that the oxygen does not appear as such but unites with the carbon gradually consuming the catalyst. See: *The Production of Hydrochloric Acid from Chlorine and Water.* GIBBS, *J. Ind. and Eng. Chem.,* **12,** 538 (1920).—H. D. GIBBS.

[28] WOOG, *Compt. rend.,* **145,** 124 (1907); *C. A.,* **1,** 2690.

[29] SABATIER and MAILHE, *Compt. rend.,* **142,** 1394 (1906); *C.,* **1906,** (2), 402.

which is the real agent when copper is used, as has been said above. Sabatier and Mailhe have shown that the oxides of copper, nickel, and cobalt, as well as those of chromium, manganese, uranium, etc., have catalytic properties entirely comparable to those of finely divided platinum. When these oxides are heated to 200° in a mixture of oxygen with the vapors of aliphatic hydrocarbons (methane, pentane, hexane, and heptane), they become incandescent and maintain themselves so, giving mainly water and carbon dioxide, but also a certain amount of aldehyde and acid.[29]

Almost simultaneously with the above work, Matignon and Trannoy have shown the possibility of realizing a *lamp without flame* by the aid of asbestos fibers impregnated with the oxides of iron, nickel, chromium, copper, manganese, cerium, and silver suspended in a mixture of air and ether vapor.[30]

The use of ferric oxide between 175 and 300° permits the regular oxidation of toluene to benzaldehyde; the most favorable temperature is 280° and the yield of aldehyde may reach 20%. Above 280° the oxide becomes incandescent and there is partial charring of the products.

Employed in the same way, nickel oxide gives benzaldehyde above 150°, while at 270° incandescence begins to manifest itself.

With copper oxide (oxidised turnings), the reaction takes place between 180 and 260°.[31][32]

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[30] MATIGNON and TRANNOY, *Compt. rend.,* **142**, 1210 (1906); *C.,* 1906 (2), 202.

[31] WOOG, *Compt. rend.,* **145**, 124 (1907), *C. A.,* **1**, 2690.

[32] The catalytic oxidation of carbon monoxide at low temperatures may be brought about by certain metals such as platinum and palladium but the time of contact necessary for complete oxidation is quite great. Mixtures of certain metallic oxides are much more effective and may bring about the catalytic oxidation of carbon monoxide at room temperatures with a surprisingly short time of contact. These mixed-oxide catalysts require careful preparation in order that they may function under these conditions. Fineness of subdivision and intimacy of admixture of the ingredients are among the most essential conditions. The most important of this class of catalysts for the oxidation of carbon monoxide contains, as its essential constituent, manganese dioxide made by the method of Frémy (Compt. rend., **82**, 1213 (1876). Copper oxide or silver oxide, when properly incorporated with this manganese dioxide, gives an excellent catalyst which is capable of effecting the catalytic oxidation with great rapidity even at temperatures somewhat below 0° C.

To prepare the catalyst, the Frémy oxide is washed free of sulphates and filtered on a Büchner funnel. This paste, usually containing about 60% of water, is analyzed for moisture by drying to constant weight at 130° in oxygen. A weighed amount of this paste is mixed with a large volume of cold water, care being taken to secure a uniform suspension. To this suspension is added such

260. *Vanadium pentoxide* is also a very active oxidation catalyst and can transform the vapors of ethyl alcohol mixed with air into acetaldehyde and acetic acid.[33] Acetaldehyde can also be changed to acetic acid; this oxidation is readily realized by passing a current of air through a solution of the aldehyde in glacial acetic acid containing oxides of vanadium,[34] uranium[35] and iron.[36]

261. Cerium oxide also can be employed for transforming acetaldehyde into acetic acid (256). The aldehyde mixed with 1% cerium oxide is submitted to the action of oxygen at two atmospheres or of air at higher pressures. The oxidation evolves heat and gives a yield of 95%.[37]

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an amount of a solution of copper or silver nitrate, as the case may be, as will give a mixture of 75% of manganese dioxide to 25% of the other oxide and, with continual vigorous stirring, a solution of sodium carbonate is run in till precipitation is just complete. The precipitate is filtered, carefully washed, and thoroughly dried at about 130°. In order to produce a harder and less friable product, it is well to compress the material in a filter press before drying. Silver oxide may be precipitated by caustic soda, but with copper, sodium carbonate must be used, the copper carbonate passing into the oxide during the drying. Both silver and copper oxides may be used in the catalyst. Certain other oxides, such as iron oxide, may be tolerated in limited amounts and appear to act only as diluents. When properly prepared, these catalysts will bring about the complete oxidation of carbon monoxide provided a sufficient amount of oxygen is present in the mixture. Moisture is rapidly absorbed by the catalyst, diminishing its activity, hence the gas mixture must be relatively dry for the oxidation to be catalytic. — J. C. W. FRAZER.

[33] NAUMANN, MOESER, and LINDENBAUM, *J. prakt. Chem.* (2), **75**, 146 (1907).

[34] Vanadium pentoxide is an excellent catalyst for the oxidation of toluene to benzaldehyde, anthracene to anthraquinone, naphthalene to phthalic anhydride and other reactions of a similar nature.

Phthalic anhydride is produced in America almost exclusively by this process. Naphthalene is volatilized in an air stream and passed over the catalyst. The reaction begins at about 300° and attains a maximum yield at about 400 to 450°, equaling about 50% of the theoretical. [GIBBS, *J. Ind. Eng. Chem.*, **11**, 1031 (1919)].

Vanadium compounds have been extensively employed in the production of aniline black. [PINKNEY, *Brit. pat.* 2745 of 1871, See *Chem. News*, **33**, 116 (1876)].

Austerweil (U. S. pat. 979,247 (1910); *C. A.*, **5**, 972) used vanadium compounds in solution to catalyze the oxidization of borneol to camphor by nitric acid. — H. D. GIBBS.

[35] Recently the oxidation of benzene vapors by air in the presence of vanadium pentoxide has assumed commercial importance as a method for manufacturing maleïc acid, WEISS and DOWNS, *J. Ind. Eng. Chem.*, **12**, 228 (1920), *U. S. patents* 1,318,631-2-3, Oct. 14, 1919, *C. A.*, **14**, 70; *Can. pat.* 192,766, Sept. 16, 1919, *C. A.*, **13**, 2683. — E. E. R.

[36] JOHNSON, *English patent* 17,424 of 1911; *J. Soc. Chem. Ind.*, **31**, 772 (1912).

[37] FARBW. MEISTER, LUCIUS and BRÜNING, *English patent* **10,377** of 1914, *J. Soc. Chem. Ind.*, **33**, 961 (1914).

The use of cerium oxide permits *acetic acid* being made from *acetylene* in one operation by effecting the hydration (309) and oxidation simultaneously. It is sufficient to circulate a mixture of 130 parts acetylene and 80 to 100 parts oxygen through a mixture of 400 parts glacial acetic acid, 100 parts water, 50 parts mercuric nitrate, and 10 parts cerium oxide kept between 50 and 100°.[38]

262. *Anthracene* can be transformed directly into anthraquinone by gaseous oxygen under pressure and in the presence of catalysts.[39] *Osmium* peroxide in the small amount of 0.05% realizes this oxidation rapidly with oxygen under 10 atmospheres pressure.[40] The same result can be obtained by keeping anthracene suspended in 30 parts water containing a little ammonia and 0.5 part copper oxide for 20 hours at 170° with compressed oxygen.[41]

The mixture of oxides remaining from the manufacture of Welsbach incandescent mantles has been proposed as a catalyst for direct oxidation.[42]

263. **Metallic Chlorides.** *Anhydrous aluminum chloride,* $AlCl_3$, causes the direct fixation of atmospheric oxygen by aromatic hydrocarbons. Benzene gives a certain amount of phenol and toluene yields *m.*cresole.[43]

264. **Manganous Salts.** As has been stated in Chapter III (153), *manganous salts* are active agents of direct oxidation, particularly in water solution. This activity persists whatever be the acid constituent of the salt; it is observed in the salts of mineral acids, in the acetate, butyrate, benzoate and oxalate: it is sixteen times as great in the succinate as in the nitrate. We can assume that the manganous salt is partially hydrolyzed in water solution and that the resulting manganous hydroxide is oxidised to the dioxide by one atom of an oxygen molecule, the other oxidising the organic compound. The nascent manganese dioxide, in turn, would part with its extra oxygen to another portion of the organic compound and the manganous hydroxide thus regenerated would begin the cycle again. A trace of the manganous salt would thus be able to oxidise an unlimited amount of the oxidisable substance.[44]

[38] DREYFUS, *French patent* 479,656, *J. Soc. Chem. Ind.,* **35,** 1179 (1916).

[39] The best catalyst yet found for oxidising anthracene to anthraquinone is vanadic oxide. The conditions are about the same as for the oxidation of naphthalene to phthalic anhydride. — H. D. GIBBS.

[40] HOFMANN, *Berichte,* **45,** 3329 (1912).

[41] *German patent,* 292,681.

[42] MASON and WILSON, *Proc. Chem. Soc.,* **21,** 296 (1905); *C.,* **1906** (1), 395.

[43] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), **14,** 435 (1888).

[44] BERTRAND, *Bull. Soc. Chim.* (3), **17,** 753 (1897).

Cerium salts may frequently act similarly (153).

265. Oxidation of Oils.   The *bleaching* of oils can be effected by a moderate oxidation with warm air in the presence of catalytic oxides which doubtless act after being transformed into *metallic soaps*, the true decolorizers.

Palm oil through which a current of air is passed at 80–90° is bleached in four hours if 0.2% *manganese borate* is added.   The same oil with 0.1% *cobalt borate* is bleached in 3.5 hours by the passage of less than its own volume of air.   With the same proportion of *nickel* or *iron borate*, about three times as much air and 10 hours are required.[45]

If the operation is carried on in an autoclave with compressed air, the addition of 0.02% of cobalt soap permits various oils to be bleached perfectly and rapidly.[46]

266. The so-called drying oils, such as linseed and poppy seed, have the property of rapidly becoming thick in contact with air, which oxidises them, converting them into resinous substances which are almost insoluble in boiling alcohol.   It has long been known that this *drying power*, depending on the oxidisability, is greatly increased by incorporating with the oils small proportions of salts of *lead* and particularly of *manganese*, the important accelerating agent appearing to be the metallic soap formed with the oil.[47]

The metallic soaps that are the most active are those containing metals which are capable of several degrees of oxidation, particularly, *cobalt, manganese, cerium, lead, chromium, iron,* and *uranium*, while soaps containing bismuth, aluminum, mercury, and thallium are less active.[48]

The direct oxidation of oils is retarded by moisture and accelerated by light.   Elevation of temperature and increase of the pressure of the oxygen increase the velocity of the oxidation.[49]

267. Metallic Silicates.   Silicates can sometimes be substituted for the corresponding oxides.   Kaolin (aluminum silicate) causes the union of hydrogen and oxygen at 230°.[50]

[45] Sastry, *J. Chem. Soc.*, **107**, 1828 (1916).
[46] Rai, *J. Soc. Chem. Ind.*, **36**, 948 (1917).
[47] Livache, *Compt. rend.*, **124**, 1520 (1897); *C.*, **1897** (2), 332.
[48] Mackey and Ingle, *J. Soc. Chem. Ind.*, **36**, 317 (1917).
[49] Fokin, *Z. angew. Chem.*, **22**, 1451 (1909).
[50] Joannis, *Compt. rend.*, **158**, 501 (1914); *C. A.*, **9**, 1866.

II. — Oxidations Carried Out with Oxidising Agents

268. Oxidations by Hydrogen Peroxide. The oxidation of organic compounds by hydrogen peroxide can be advantageously catalyzed by small quantities of *ferrous* or *ferric salts* (acetate).[51]

Methyl, ethyl, propyl, butyl, isobutyl, and *isoamyl alcohols* are oxidised to a mixture of aldehyde and acid, the acid being more abundant when ferrous oxalate is used than with the sulphate. The addition of wood charcoal favors the production of aldehyde. Manganous salts can be substituted for the iron.[52]

Glycol furnishes *glycolic aldehyde* without any *glyoxal.*[53] *Glycerine* reacts vigorously to give *glyceric aldehyde,* along with a little *dihydroxy-acetone.*[54] *Arabite* yields an *araboketose* and *dulcite, galactose.*[55] *Malic acid* passes into *oxalacetic acid,* $HO_2C.CO.CH_2.CO_2H.$[56]

Benzene is partially transformed into *phenol* and then to *pyrocatechol;*[57] *p.hydroxybenzaldehyde,* $HO.C_6H_4.CHO,$ gives *protocatechuic aldehyde.*[58]

Amines likewise undergo a regular oxidation to the corresponding aldehydes when they are warmed above 50° with hydrogen peroxide in presence of a ferrous salt; *ethylamine* giving *acetaldehyde; isoamylamine, isovaleric aldehyde; benzylamine, benzaldehyde,* while *aminoethyl alcohol* is changed, above 30°, to a mixture of *glycolic aldehyde* and *glyoxal.*[59]

The use of the double cyanide of copper and potassium permits the oxidation of morphine hydrochloride by hydrogen peroxide to *dehydromorphine* and *pseudomorphine.*[60]

Furfural in alcoholic beverages can be destroyed slowly by the addition of 1% *hydrogen peroxide* and 0.01% *manganese acetate.*[61]

269. Oxidation by Nitric Acid. *Vanadium pentoxide,* employed

[51] FENTON, *J. Chem. Soc.,* **65**, 899 (1894).

[52] DOROSHEVSKII and BARDT, *J. Russian Phys. Chem. Soc.,* **46**, 754 (1914); *C. A.,* **9**, 1865.

[53] FENTON and JACKSON, *J. Chem. Soc.,* **75**, 575 (1899).

[54] FENTON and JACKSON, *Ibid.,* **75**, 1 (1899).

[55] NEUBERG, *Berichte,* **35**, 962 (1902).

[56] FENTON and JONES, *J. Chem. Soc.,* **77**, 69 (1900) and **79**, 91 (1901).

[57] CROSS, BEVAN and HEIBERG, *Berichte,* **33**, 2015 (1900).

[58] SOMMER, *German patent,* 155,731, *C.,* **1904** (2), 1631.

[59] SUTO, *Biochem. Zeitschr.,* **71**, 169 (1915); *C. A.,* **9**, 3059.

[60] DENIGÈS, *Bull. Soc. Chim.* (4), **9**, 264 (1911).

[61] CHAUVIN, *Ann. Falsif.,* **6**, 463 (1913); *C. A.,* **8**, 981.

in the ratio of 0.1 g. to 50 g. *cane sugar* and 500 cc. nitric acid (density 1.4) causes the complete oxidation of the sugar in 20 to 30 hours in the cold to *oxalic acid* without the formation of saccharic, mucic, tartaric acids, etc., as by-products. Above 70°, carbon dioxide and water are obtained instead of oxalic acid.[62]

In the presence of *mercuric nitrate,* nitric acid oxidises anthracene to *anthraquinone.* The reaction is finished in three hours if 117 parts anthracene suspended in 300 parts nitrobenzene are warmed to 30° with 460 parts 31% nitric acid in which three parts of mercury have been dissolved.[63]

In the nitration of aromatic compounds by mixtures of nitric and sulphuric acids, the presence of a mercuric salt has no influence, but with nitric acid of density 1.3, it causes oxidation along with nitration or the substitution of a nucleus hydrogen by the phenolic hydroxyl group. Thus benzene, toluene, and ethyl-benzene give nitrophenols. It is possible to prepare 2,4-dinitrophenol and picric acid by heating benzene on the steam bath under reflux with 8 times its weight of nitric acid, density 1.3, and 15% mercuric nitrate. The oxidation must precede the nitration, since nitrobenzene is not oxidised by this treatment.[64] [65]

[62] NAUMANN, MOESER, and LINDENBAUM, *J. prakt. Chem.* (2), **75,** 148 (1907).

[63] *U. S. patent,* 119,546.

[64] WOLLFENSTEIN and BÖTERS, *Berichte,* **46,** 586 (1913).

[65] In addition to vanadium and mercury compounds, a number of other substances have been found to accelerate oxidation by nitric acid. Disregarding the mechanism of reaction, oxides of nitrogen and nitrous acid may be considered as catalysts for oxidation by nitric acid. For instance, VELEY (*Proc. Roy. Soc.,* **48,** 458–9 (1891)) found that the presence of nitrous acid initiated the oxidation of copper, mercury and bismuth by 30% nitric acid. Oxides of nitrogen are mentioned a number of times in the patent literature as being necessary or desirable for the purpose of starting oxidation of organic compounds by nitric acid, especially in the manufacture of camphor. Molybdenum compounds, salts of manganese, iron, cerium and palladium, and even salts of calcium and magnesium have, under various conditions, been found to accelerate oxidations by nitric acid. Probably, in many cases, the acceleration produced by foreign substances is due to the reducing action of the substance on the nitric acid, with consequent formation of oxides of nitrogen. Thus the Commercial Research Company proposes to start the oxidizing action of nitric acid on aromatic hydrocarbons with side chains by means of formaldehyde, copper, zinc, starch or other reducing substance (*Brit. Pat.,* 141,333 (1920)).

Nitration by means of nitric acid is likewise accelerated by dissolved oxides of nitrogen. KLEMENC and EKL (*Monatsh.* **39,** 641–98 (1918)) studied the nitration of a number of phenol derivatives and concluded that pure nitric acid, free from dissolved nitrogen peroxide or nitrous acid, does not cause nitration.

HOLDERMANN (*Berichte,* **39,** 1250 (1906)) obtained negative results in efforts to influence the position of the entering nitro-groups by nitrating in the pres-

270. Oxidations by Hypochlorites. The addition of a very small amount of a cobalt or nickel salt to a solution of an alkaline hypochlorite, or chloride of lime, causes the evolution of oxygen in the cold.[66]

This oxidising mixture may be used for oxidising organic substances. It transforms *o.nitrotoluene* into *o.nitrobenzaldehyde* and *acid.*[67]

By the same means, phenanthridene is oxidised to phenanthridone: [68]

$$
\begin{array}{ccc}
\begin{array}{c} C_6H_4 - CH \\ | \quad\quad || \\ C_6H_4 - N \end{array}
& \rightarrow &
\begin{array}{c} C_6H_4 - CO \\ | \quad\quad | \\ C_6H_4 - NH \end{array}
\end{array}
$$

and acridine into acridone:

$$
C_6H_4 \underset{\diagdown N \diagup}{\overset{\diagup CH \diagdown}{\big|}} C_6H_4 \quad \rightarrow \quad C_6H_4 \underset{\diagdown NH \diagup}{\overset{\diagup CO \diagdown}{}} C_6H_4
$$
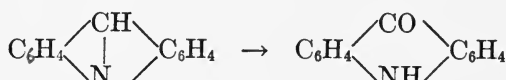
271. Oxidations by Chlorates. The oxidation of aniline hydrochloride, in the preparation of aniline black, is carried out in the cold by a solution of potassium or sodium chlorate with the aid of metal catalysts, the most active of which is *vanadium pentoxide*, V_2O_5, of which one part is sufficient for 270,000 parts of aniline and the corresponding amount of chlorate. Salts of *cerium* and, to a less extent, those of *copper* and *iron* are useful catalysts but less powerful.

Osmium peroxide, OsO_4, is at least as powerful as vanadium pent-

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ence of catalysts, but an appreciably greater yield of dinitrobenzene, from nitrobenzene, was obtained by nitrating with, rather than without, a small amount of mercuric nitrate, under conditions otherwise similar (28.0% and 23.5% of theory respectively). Also, Holdermann obtained evidence that mercuric nitrate acts as catalyst in the nitration of beta-methylanthraquinone. For the control of the position of the entering nitro-group, the use of considerable quantities of different acids mixed with the nitric acid is more promising than the use of small amounts of metal salts. See TINGLE and BLANCK (*J. Amer. Chem. Soc.*, **30**, 1395 and 1587 (1908)).

Additional data on simultaneous nitration and oxidation in the presence of mercury compounds are given by WOLFFENSTEIN and PAAR (*Berichte*, **46**, 589 (1913)) and VIGNON (*Bull. Soc. Chim.*, **27**, 547–50 (1920)). There are also a number of patents on this subject. Silver, copper and aluminum salts are said to act as catalysts as well as mercury. — A. S. RICHARDSON.

[66] FLEITMANN, *Annalen*, **134**, 64 (1865).
[67] BADISCHE, *German patent*, 127,388, *C.*, **1902** (1), 150.
[68] PICTET and PATRY, *Berichte*, **26**, 1962 (1893).

oxide and its use makes it possible to oxidise *anthracene* to anthraquinone by means of chlorates.[69]

272. Oxidations by Sulphur Trioxide. Fuming sulphuric acid is frequently used as an oxidiser for organic compounds, the trioxide being reduced to the dioxide, but its action is not rapid enough in the absence of metallic catalysts, the most active being mercuric sulphate between 290 and 390°.[70] The sulphates of potassium, magnesium, manganese, and cobalt are without effect, while those of nickel and iron act feebly. Only the *sulphate* of *copper* can replace that of mercury in practice but it is disadvantageous. It should be mentioned that a mixture of the sulphates of copper and mercury is more active than the two taken separately.[71]

It has been proposed to add to the sulphuric acid the mixture of the rare earths (oxides of cerium, lanthanium, etc.) which is a by-product in the manufacture of thorium nitrate, but this has not proved to be of any advantage.[72]

In the Kjeldahl method for estimating nitrogen in organic compounds, the substances are boiled for a long time with fuming sulphuric acid. During the oxidation of the carbon and hydrogen, all the nitrogen passes into ammonia which is retained by the sulphuric acid without being burned. The addition of 0.5% mercuric sulphate triples the speed of the oxidation.[73] In practice, 1 to 2 g. of mercury to 20 cc. acid is used for 5 to 7 g. of sample to be analyzed.

273. The chief application of oxidation by fuming sulphuric acid is the preparation of *phthalic acid* from *naphthalene*, a reaction which is the basis of one of the methods for making artificial indigo.[74] When naphthaline is moderately heated with the acid, sulphonation takes place, but above 200° oxidation sets in. At 275° the oxidation rate is quintupled by 1% of mercuric sulphate.[75]

274. In the presence of mercuric sulphate, fuming sulphuric acid can oxidise *anthraquinone* and further oxidise the hydroxyanthraquinones first formed. Thus anthraquinone and 1-hydroxyanthraquinone give quinizarine, $1,4\text{-}C_{14}H_6O_2(OH)_2$.[76]

At 200–250°, *alizarine* gives *quinalizarine*, $1,2,5,8\text{-}C_{14}H_4O_2(OH)_4$,

[69] HOFMANN and SCHUMPELT, *Berichte*, **48**, 816 (1915).

[70] GRAEBE, *Berichte*, **29**, 2806 (1896).

[71] BREDIG and BROWN, *Z. physik. Chem.*, **46**, 502 (1903).

[72] DITZ, *Chem. Zeit.*, **29**, 581 (1905); *C.*, **1905** (2), 485.

[73] WILFARTH, *Chem. Centr.*, **1885**, 17 and 113.

[74] BADISCHE, *German patent*, 91,202.

[75] This process is being replaced by the high temperature air oxidation process. See note to 260 *supra*. — H. D. GIBBS.

[76] WACKER, *J. prakt. Chem.* (2), **54**, 88 (1896).

and 1,3,5,7-tetrahydroxyanthraquinone heated with 20 parts of sulphuric acid of 66° Bé. to the same temperature in the presence of 0.05 part mercuric sulphate, yields 1,3,4,5,7,8-hexahydroxyanthraquinone or *anthracene blue*. The addition of *boric acid* greatly favors these reactions.

275. Oxidations by Permanganates. The oxidation of aliphatic alcohols by potassium permanganate in presence of ferrous sulphate readily gives *aldehydes* but, on the contrary, in the presence of ferrous oxalate, the *acids* are formed quantitatively.[77]

276. Oxidations by Persulphates. The *persulphates* of the *alkalies* mixed with nitric acid and a small quantity of *silver nitrate* are useful for oxidising organic compounds. The active agent is a silver *peroxide* or *pernitrate* which is constantly regenerated by the persulphate.[78]

Benzene is transformed into *quinone* by this means, and *oxalic acid* is burned to carbon dioxide. *Quinone* is broken up into a number of products among which is found *maleïc acid*.[79]

277. Oxidations by Nitrobenzene. In the dye industry *nitrobenzene* is frequently used as an oxidising agent, being reduced to aniline; the presence of ferrous salts aids in these oxidations.

[77] Doroshevskii and Bardt, *J. Russian Phys. Chem. Soc.*, **46**, 754 (1914); *C. A.*, **9**, 1865.

[78] Kempf, *Berichte*, **38**, 3963 (1905). Baborovsky and Kuzma, *Z. Elektroch.*, **14**, 196 (1908).

[79] Kempf, *Berichte*, **39**, 3715 (1906).

CHAPTER VI

VARIOUS SUBSTITUTIONS IN MOLECULES

§ 1. — INTRODUCTION OF CHLORINE, BROMINE AND IODINE

Chlorinations

278. The presence of anhydrous chlorides is a great aid in the direct chlorination of organic compounds, whether the chlorides are added as such or as the elements which are immediately transformed into the chlorides by the chlorine. There is no need to distinguish between these two.

Iodine or Iodine Chloride. Iodine, or iodine monochloride, in presence of an organic substance and of chlorine is changed to the trichloride which gives up chlorine to the organic substance, being itself reduced to the monochloride which starts all over again. With 2 to 12% of iodine it is easy to chlorinate *benzene*,[1] *toluene*,[2] the *xylenes*,[3] etc., and also to transform *carbon disulphide* into carbon tetrachloride.[4][5]

The chlorine compounds thus obtained are always mixed with a small amount of iodine derivatives formed by catalytic induction.

279. **Bromine.** This can catalyze chlorinations in the same manner as iodine, particularly in the preparation of carbon tetrachloride from the disulphide, but its use is less advantageous.

280. **Sulphur.** The immediate chlorination of sulphur by chlorine to several degrees of chlorination makes of it a good chlorinating agent of moderate activity which gives excellent results in some cases. Thus to transform *acetic acid* into chloracetic, chlorine is

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[1] Müller, *J. Chem. Soc.*, **15**, 41 (1862); *Jahresb.*, **1862**, 414 and **1864**, 524. Jungfleisch, *Ann. Chim. Phys.* (4), **15**, 186 (1868).

[2] Beilstein and Geitner, *Annalen*, **139**, 334 (1866). Limpricht, *Ibid.*, **139**, 326 (1866). Hübner and Majert, *Berichte*, **6**, 790 (1873).

[3] Wollrath, *Zeit. f. Chem.*, **1866**, 488. Krüger, *Berichte*, **18**, 1755 (1885). Kluge, *Ibid.*, **18**, 2099 (1885). Koch, *Ibid.*, **23**, 2319 (1890).

[4] *English patent*, 18,890 of 1899.

[5] With iodine as a catalyst, the reaction may be stopped at the intermediate stage, Cl_3CSCl, though with iron, carbon tetrachloride is formed at once. (Helfrich and Reid, *J. Amer. Chem. Soc.*, **43**, 593 (1921)). — E. E. R.

passed into the boiling acid containing a small amount of sulphur. In two hours 8 parts of acetic acid are changed to 10 parts chloracetic containing but little acetyl chloride. In the cold, with a little sulphur or sulphur chloride, only *acetyl chloride* is obtained.[6]

281. **Phosphorus.** Red phosphorus can be substituted for sulphur in the preparation of chloracetic acid (280).

The presence of *phosphorus trichloride* greatly facilitates the formation of *benzyl chloride* from toluene. By passing a current of chlorine into 100 parts of boiling toluene containing 1 part phosphorus trichloride (as far as possible in the sunlight),[7] 80 parts of the desired product are obtained in eight hours.

282. **Charcoal.** *Wood charcoal* readily causes the chlorination of hydrogen to hydrochloric acid without explosion. By passing a mixture of equal volumes of carbon monoxide and chlorine through a long tube filled with fragments of charcoal, carbonyl chloride is obtained.[8] *Animal black* gives even better results, a 30 cm. tube being sufficient.[9] [10]

A charcoal made by calcining blood with potassium carbonate can serve as a catalyst for the chlorination of organic substances between 250° and 400°. The progressive and complete chlorination of ethyl chloride can thus be readily obtained.[11]

Carbon can likewise serve as a catalyst in the preparation of *carbon tetrachloride* from *carbonyl chloride* by a kind of auto-chlorination:

$$2COCl_2 = CO_2 + CCl_4 \cdot$$

The carbonyl chloride vapors are passed through a succession of towers filled with *coke* or *animal charcoal*.[12]

[6] AUGER and BÉHAL, *Bull. Soc. Chim.* (3), **2**, 145 (1889). RUSSANOF, *J. Russian Phys. Chem. Soc.*, **1891**, 1, 222; *Berichte*, **25**, Ref. 334 (1892).

[7] If sunlight is used no other catalyst is required. The chlorine reacts as fast as it can be passed in, even at 0°. — E. E. R.

[8] SCHIEL, *Jahresb.*, **1864**, 359.

[9] PATERNO, *Gaz. Chim. Ital.*, **8**, 233 (1878).

[10] Using 10 g. charcoal prepared from ox bones, ATKINSON, HEYCOCK and POPE (*J. Chem. Soc.*, **117**, 1410 (1920)) caused carbon monoxide and chlorine to combine at 40 to 50° as rapidly as the mixture could be passed into the U-tube containing the catalyst. After the preparation of 10 k. of phosgene this catalyst had lost none of its activity.

They found the activated charcoal from Army box respirator to be more active still, it being extremely efficient even at 14°. Even at 50° this catalyst does not cause the formation of hydrogen chloride in mixtures of chlorine and carbon monoxide containing hydrogen. — E. E. R.

[11] DAMOISEAU, *Compt. rend.*, **83**, 60 (1876).

[12] *U. S. patent*, 808,100.

283. Metallic Chlorides.   Activity is possessed by the chlorides of polyvalent metals which have several degrees of chlorination, such as iron, thallium, molybdenum, antimony, tin, gold, vanadium, uranium, etc., and also by aluminum chloride and to a certain extent by zinc chloride but not by the chlorides of the alkaline or alkaline earth metals or of nickel, cobalt, manganese or lead.[13]

Moisture is usually unfavorable to their action.

284. Aluminum Chloride.   Anhydrous aluminum chloride, or *aluminum* turnings, is an excellent chlorination catalyst.[14]   It readily realizes the transformation of carbon disulphide into carbon tetrachloride.[15]   The addition of 3% of it to benzene permits the progressive introduction of chlorine, going from the monochlor- to hexachlorbenzene.[17]

A mixture of equal volumes of chlorine and *carbon monoxide* passed over fragments of anhydrous aluminum chloride at 30–35°, is partially transformed into phosgene.   The yield is better when the mixture of the gases is passed into chloroform saturated with aluminum chloride.[18]

285. Ferric Chloride.   A little *ferric chloride,* for which may be substituted iron scale, iron sesquioxide or sulphide, ferrous carbonate, or even iron sulphate, gives good results with the substitution of chlorine in aromatic compounds.

By using one part ferric chloride and one of iron powder to 300 parts of benzene, one obtains a yield of 335 parts of monochlorbenzene with 37 parts of poly-chlor-.[19] [20]

[13] Willgerodt, *J. prakt. Chem.* (2), **34**, 264 (1886) and **35**, 391 (1887).

[14] Seelig, *Annalen,* **237**, 178 (1887).

[15] Goldschmidt and Larsen, *Z. physik. Chem.,* **48**, 424 (1904).   Bornwater and Holleman, *Rec. Trav. Chim. Pays-Bas,* **31**, 221 (1912).

[16] Mouneyrat, *Bull. Soc. Chim.* (3), **19**, 262 (1898).

[17] Mouneyrat and Pouret, *Compt. rend.,* **127**, 1026 (1898); *C.,* 1899 (1), 199.

[18] Plotnikov, *J. Russian Phys. Chem. Soc.,* **48**, 457 (1916).

[19] Fahlberg, List & Co., *German patent,* 219,242.

[20] It is usually assumed that the action of ferric chloride depends on the polyvalency of iron, supposing that a part of its chlorine is abstracted by the benzene leaving ferrous chloride which then combines with free chlorine to regenerate the ferric chloride.

In order to find whether benzene actually takes chlorine away from ferric chloride the following experiments were tried in my laboratory by H. K. Parker. Ferric chloride was sublimed, as it was formed, into a dry flask which was repeatedly evacuated to remove free chlorine.   To this ferric chloride, 100 g. of benzene was added and kept at 40° for 30 hours, after which water was added. No chlorine was found in the benzene layer.   The water layer contained 2.90 g. ferric chloride and 0.36 g. ferrous.   Into a similar mixture of ferric chloride and benzene, dry chlorine was passed at 40° for 2 hours and extensive chlorination

It is equally satisfactory for the chlorination of toluene [21] or the xylenes.[22]

The use of ferric chloride facilitates the commercial preparation of *carbon tetrachloride* from carbon disulphide:

$$CS_2 + 3\,Cl_2 = S_2Cl_2 + CCl_4$$
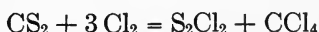
because it catalyzes the chlorination of the carbon disulphide by the sulphur chloride according to the equation:

$$CS_2 + 2\,S_2Cl_2 = 6\,S + CCl_4.$$
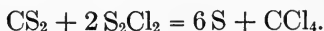
The reaction commences at 60° and is continued at the boiling temperature of the mixture.[23] [24]

286. Molybdenum Chloride. Molybdenum chloride, $MoCl_5$, is an excellent catalyst in the *aromatic series* and, when used to the amount of 0.5%, permits successive stages of chlorination. Its use is of no advantage in the aliphatic series.[25]

287. Antimony Chlorides. The chlorides of antimony (which can be replaced by the powdered metal or by the oxide) are frequently employed as carriers in chlorinations. They are more active than iodine and permit the complete chlorination of benzene.[26]

They are useful in transforming carbon disulphide into the tetrachloride.[27]

The successive use of *iodine* and of *antimony pentachloride* enables us to pass directly from benzyl chloride to *hexachlor-* and *heptachlortoluene*.[28]

288. Tin Chloride. Stannic chloride (which can be replaced by the metal or the oxide) can also give good effects.[29] Its action, as

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took place. At the end there was 30 g. benzene still unchlorinated and treatment with water showed only 0.04 g. ferrous iron.

These experiments show that the reduction of ferric chloride by a large excess of benzene is very slight. It seems to me best to regard the action of ferric chloride as analogous to that of aluminum chloride in this reaction, see note to 157.—E. E. R.

[21] Seelig, *Annalen,* **237,** 152 (1887).

[22] Claus and Burstert, *J. prakt. Chem.* (2), **41,** 552 (1890).

[23] Müller and Dubois, *German patent,* 72,999. *English patent,* 19,628 of 1893.

[24] With iron as catalyst, it is impossible to stop at the intermediate, $Cl_3CSCl.$—E. E. R.

[25] Aronheim, *Berichte,* **8,** 1400 (1875). Seelig, *Annalen,* **237,** 152 (1887).

[26] Müller, *Zeit. Chem. Pharm.,* **1864,** 40.

[27] Hofmann, *Annalen,* **115,** 264 (1860).

[28] Beilstein and Kuhlberg, *Annalen,* **150,** 306 (1869).

[29] Pétricou, *Bull. Soc. Chim.* (3), **3,** 189 (1890).

without doubt is the action of all chlorides used to aid direct chlorinations, is proportional to its concentration.[30]

289. Aluminum Bromide. Its use permits the direct preparation of *perchlorethane*, $CCl_3 . CCl_3$, starting with acetylene tetrabromide, $CHBr_2 . CHBr_2$, or with ethylene bromide.[31]

Brominations

290. Anhydrous chlorides and bromides are more or less active agents in bromination just as in chlorination. The *hydrobromic acid* produced in the reaction is the product most readily followed.[32]

291. Iodine. Iodine, or rather iodine bromide, which is the immediate product, is frequently used and leads especially to the bromination of the aromatic nucleus.[33]

292. Manganese. Powdered metallic manganese is an excellent catalyst for the bromination of benzene, toluene, and xylene. With 3 g. of the powdered metal and bromine, 18 g. benzene is completely converted into monobrombenzene in 90 hours in the cold, without the metal suffering any appreciable attack.[34] The slight traces of bromide formed on the surface are doubtless sufficient to catalyze the reaction.

293. Aluminum Chloride. A small proportion is sufficient to effect the regular bromination of most organic compounds. Thus 1 g. can cause the bromination of 120 g. benzene.[35]

We may put alongside of the brominations catalyzed by aluminum chloride the migration, which it causes, of the bromine of tribromphenol to benzene,[36] or toluene,[37] which are thereby transformed to brombenzene or *m*.bromtoluene with the production of phenol.

Aluminum bromide causes a regular bromination of toluene.[38]

Zinc Chloride and Bromide. Zinc chloride or metallic zinc which is changed to the bromide may be effective.[39]

[30] GOLDSCHMIDT and LARSEN, *Z. physik. Chem.*, **48**, 424 (1904).

[31] MOUNEYRAT, *Bull. Soc. Chim.* (3), **19**, 262 (1898).

[32] GUSTAVSON, *J. prakt. Chem.* (2), **62**, 281 (1900).

[33] RILLIET and ADOR, *Berichte*, **8**, 1287 (1875). JACOBSEN, *Ibid.*, **17**, 2372 (1884) and **18**, 359 (1885). BRUNER, *Chem. Cent.*, **1900** (2), 257.

[34] DUCELLIEZ, GAY, and RAYNAUD, *Bull. Soc. Chim.* (4), **15**, 737 (1914).

[35] FITTIG, *Annalen*, **121**, 361 (1862). LEROY, *Bull. Soc. Chim.* (2), **48**, 210 (1887). ROUX, *Ann. Chem. Phys.* (6), **12**, 347 (1887).

[36] KOHN and MÜLLER, *Monatsh. Chem.*, **30**, 407 (1909).

[37] KOHN and BUM, *Ibid.*, **33**, 923 (1912).

[38] GUSTAVSON, *J. Russian. Phys. Chem. Soc.*, **9**, 286 (1877).

[39] SCHIAPARELLI, *Gaz. Chim. Ital.*, **11**, 70 (1882).

Ferric Chloride or Bromide. Ferric chloride or finely divided iron (which changes to the bromide) is a good bromination catalyst.[40]

$$Cyclobutene\ bromide, \begin{matrix} CH_2 - CHBr \\ \cdot \qquad \cdot \\ CH_2 - CHBr \end{matrix}, brominates\ in\ the\ presence\ of$$

iron powder to *tetrabrombutane*, the ring being opened.[41]

Mercuric Chloride or Bromide. These may be used as brominating agents.[42] Without doubt the simultaneous formation of aluminum and mercuric bromides is the cause of the remarkable activity of *aluminum amalgam* as a bromination catalyst.[43]

Introduction of Iodine

294. The direct introduction of iodine into organic molecules is very difficult but may sometimes be accomplished by the aid of ferric chloride, as is the case with benzene. The yield of iodide thus formed is low.[44]

§ 2. — ADDITION OF SULPHUR

295. Anhydrous *aluminum chloride* can cause the addition of sulphur to benzene at 75–80°. Thiophenol, $C_6H_5 . SH$, and products derived from it, phenyl sulphide and phenylene sulphide, are thus obtained.[45]

296. The direct sulphuration of *diphenylamine*, by heating the amine with sulphur, requires a temperature of 200 to 265° for 6 to 8 hours: [46]

$$NH \begin{matrix} \diagup C_6H_5 \\ \diagdown C_6H_5 \end{matrix} + 2S = H_2S + S \begin{matrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6M_4 \diagup \end{matrix} NH.$$
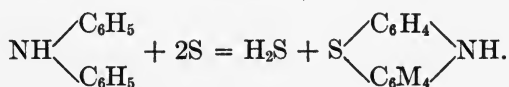
In the presence of iodine the reaction is complete in 10 minutes at 185°, giving a quantitative yield of thiodiphenyl-amine instead of 50 to 60%. Thiodinaphthyl amines, etc., are also prepared in good yields.[47]

[40] SCHENFELEN, *Annalen*, **231**, 164 (1885).

[41] WILLSTÄTTER and BRUCE, *Berichte*, **40**, 3979 (1907).

[42] LAZAREW.

[43] COHEN and DAKIN, *J. Chem. Soc.*, **75**, 893 (1899).

[44] LOTHAR MEYER, *Annalen*, **231**, 195 (1885).

[45] FRIEDEL and CRAFTS, *Bull. Soc. Chim.* (2), **39**, 306 (1883).

[46] BERNTHSEN, *Annalen*, **230**, 77 (1885).

[47] KNOEVENAGEL, *J. prakt. Chem.* (2), **89**, 11 (1914).

§ 3. — ADDITION OF SULPHUR DIOXIDE

297. *Benzene* warmed with aluminum chloride absorbs sulphur dioxide readily giving *benzene sulphinic acid*, $C_6H_5 . SO_2H$.[48] The reaction is accelerated by the presence of hydrochloric acid and is doubtless due to the formation of an unstable addition product which reacts with the benzene in the presence of the aluminum chloride and hydrochloric acid.[49]

§ 4. — ADDITION OF CARBON MONOXIDE

298. The direct addition of carbon monoxide to hydrocarbons is an exceptional reaction which can be realized in only a small number of cases.   However, the use of *aluminum chloride* or *bromide* makes it possible with aromatic hydrocarbons.

A mixture of carbon monoxide and hydrogen chloride is passed for several hours into benzene containing aluminum chloride and 10% *cuprous chloride* at 40 to 50°.

It can be assumed that the carbon monoxide dissolves on account of the cuprous chloride and forms formyl chloride, $H . CO . Cl$, which then reacts as an acid chloride on the benzene in the presence of aluminum chloride (891).   We have in the end:

$$C_6H_6 + CO = C_6H_5 . CHO.$$

The yield is 90%.[50]   Likewise from toluene and *aluminum chloride*, *p.*toluic aldehyde, $CH_3 . C_6H_4 . CHO$, with a yield of 73%;[51] *o.Xylene* gives, by the same method, 1,2 *dimethyl-benzaldehyde*(4).   *p.*Xylene and mesitylene give analogous results.[52]

The presence of the cuprous chloride and the hydrogen chloride seem to be superfluous and it is sufficient to cause the carbon monoxide under pressures of from 40 to 90 atmospheres to act on the benzene in the presence of aluminum chloride and a little hydrogen chloride.[53]

[48] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), **14**, 443 (1888).

[49] KNOEVENAGEL and KENNER, *Berichte*, **41**, 3315 (1908). ANDRIANOWSKI, *Bull. Soc. Chim.* (2), **31**, 199 and 495 (1879).

[50] REFORMATSKI, *J. Russian Phys. Chem. Soc.* **33**, 154 (1901); *C.*, **1901** (1), 1226.

[51] GATTERMANN and KOCH, *Berichte*, **30**, 1623 (1897) and GATTERMANN, *Ibid.*, **31**, 1149 (1898). *English patent*, 13,709 of 1897.

[52] BAYER AND CO., *Chem. Cent.*, **1898**, 932. HARDING and COHEN, *J. Amer. Chem. Soc.*, **23**, 594 (1901).

[53] *English patent*, 3,152 of 1915; *J. Soc. Chem. Ind.*, **35**, 384 (1916).

§ 5. — INTRODUCTION OF METALLIC ATOMS

Formation of Alcoholates

299. *Aluminum alcoholates* are formed by the direct action of aluminum amalgam on alcohols thoroughly freed from water.[54] But the presence of a catalyst enables them to be prepared directly from aluminum. It is sufficient to add a little *mercuric chloride, iodine* or even *ethyl iodide.* Thus ordinary absolute alcohol readily gives aluminum ethylate, $Al(OC_2H_5)_3$, a solid melting at 134° which can be isolated by distilling at 15 mm. pressure.[55]

Production of Mixed Organo-Magnesium Compounds

300. The production of mixed organo-magnesium compounds from *organic halides* is equivalent to the addition of the magnesium atom to the organic molecule:

$$Mg + RBr = Mg\diagup^{R}_{\diagdown Br.}$$
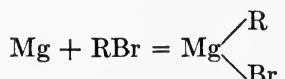
This reaction is usually carried out in *anhydrous ether* which plays the rôle of catalyst in their formation. It is possible to carry out the reaction in *benzene* in the presence of a small amount of ether. Without doubt, we have in succession:

$$RBr + (C_2H_5)_2O = \begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\diagdown O \diagup^{R}_{\diagdown Br}$$

and then:

$$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\diagdown O \diagup^{R}_{\diagdown Br} + Mg = Mg\diagup^{R}_{\diagdown Br} + O\diagup^{C_2H_5}_{\diagdown C_2H_5}$$
regenerated
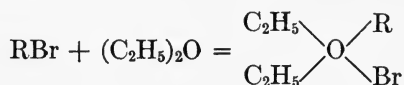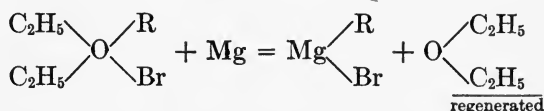
The regenerated ether can repeat the first reaction.

301. The ethyl ether as catalyst can be replaced by other ethers, *amyl ether,* etc., or even by a small quantity of a *tertiary amine* such as *dimethyl aniline,* the reaction taking place in benzene, toluene, hexane, or ligroïne. In this case the temporary addition product would be: [56]

$$\begin{array}{c} C_6H_5 \\ CH_3 \\ CH_3 \end{array}\!\!\!\! N \diagup^{R}_{\diagdown Br.}$$
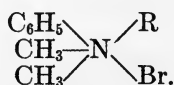
[54] Tistchenko, *J. Russian Phys. Chem. Soc.,* **31**, 483 (1899).

[55] Meister, Lucius and Brüning, *German patent,* 286,596; *J. Soc. Chem. Ind.,* **34**, 1168 (1915).   [56] Tschelinzeff, *Berichte,* **37**, 4534 (1904).

302. The formation of organo-magnesium halides is easy with *organic bromides* or *iodides* but it is greatly facilitated by the presence of a suitable catalyst, *iodine, hydriodic acid* or an *alkyl iodide* such as *ethyl iodide*.

The addition of such catalysts is indispensable for the formation of these derivatives from aliphatic or cycloaliphatic chlorides, but even with this assistance they can not be prepared from aromatic chlorides.

According to Zelinski, iodine and magnesium produce in anhydrous ether some of the compound, $MgI_2 . 2(C_2H_5)_2O$, which he was able to isolate and which would start the reaction.[57]

303. A certain number of substances hinder the formation of the organo-magnesium compounds. We may mention *anisol, ethyl acetate, chloroform*, and *carbon disulphide* which act as negative catalysts (11).

304. For the preparation of mixed organo-zinc compounds, Blaise uses pure *ethyl acetate* as a catalyst instead of ether and operates in a toluene or petroleum ether solution. Actually one-third of a molecule of ethyl acetate is used for one molecule of the alkyl iodide.[58]

[57] Zelinski, *J. Russian Phys. Chem. Soc.,* **35,** 399 (1903).
[58] Blaise, *Bull. Soc. Chim.,* 1911, Conference, 7.

CHAPTER VII

HYDRATIONS

305. HYDRATION reactions can be separated into two distinct groups according to whether the water is added without splitting the molecule or whether the addition of the water causes the original molecule to break up into two or more new ones.

As examples of the first group we have the addition of water to *unsaturated hydrocarbons* giving alcohols or ketones, or to *nitriles* and *imides*.

Reactions of the second class are more frequent, such as the *saponification* of *esters*, the decomposition of *acetals* and *glucosides*, the hydrolysis of *amides, oximes, hydrazones, semicarbazones*, etc.

More or less concentrated *mineral acids* are very powerful agents for realizing the various hydration reactions, whether in concentrated form, they give rise to unstable temporary addition products which decompose to form the hydration products and to regenerate the acids, or whether they act in dilute solution in consequence of their electrolytic dissociation, the chief factors being the hydrogen ions so liberated.

Water solutions of the strong bases, either the alkalies or alkaline earths, can often realize hydrations which water alone can usually accomplish but at a much slower rate or a much higher temperature.

1. — Fixation of Water by Addition

306. **Ethylene Compounds.** Moderately concentrated *sulphuric acid* enables us to add, in the cold, a molecule of water to *isobutylene*, $(CH_3)_2C : CH_2$, to give *trimethyl-carbinol*, $(CH_3)_3 . COH$.[1][2] By adding *amylene*, little by little, to a mixture of concentrated sulphuric acid and ice, diluting with ice water, washing with soda, and distilling the product, *dimethyl-ethyl carbinol* is obtained with a yield of 85 to 92% of the amylene.[3]

Likewise 3–methylpentene, $CH_2 : CH . CH(CH_3) . CH_2 . CH_3$, adds water to give the corresponding tertiary alcohol.

[1] BUTLEROW, *Annalen*, **144**, 22 (1867).

[2] Isopropyl alcohol is now manufactured by absorbing in sulphuric acid the propylene from the gases resulting from the cracking of heavy hydrocarbons. — E. E. R.

[3] ADAMS, KAMM, and MARVEL, *J. Amer. Chem. Soc.*, **40**, 1950 (1918).

With 85% sulphuric acid *hexene*–1 and *heptene*–3 give the secondary alcohols, accompanied by a certain amount of the *sulphuric acid esters,* while the 100% acid only polymerizes the hydrocarbons.[4]

At 45° sulphuric acid effects the addition of water to *iso-oleïc acid* which is changed to *hydroxystearic acid.*[5]

307. Dilute *nitric acid* provokes the rapid hydration of *pinene,* $C_{10}H_{16}$, in alcohol solution, at the ordinary temperature to form terpine, $C_{10}H_{20}O_2$.[6]

Hydrochloric acid also can cause the addition of water. By digesting for three hours in the light a mixture of *croton aldehyde,* $CH_3 . CH : CH . CHO$, and hydrochloric acid, the aldol, β-hydroxybutyric aldehyde, $CH_3 . CH(OH) . CH_2 . CHO$, is formed.[7]

308. Doubly Unsaturated Compounds. *Acetylene* hydrocarbons and their *allenic* isomers can add water in the presence of sulphuric acid and other catalysts to give *ketones:*

$$R.C \vdots C.R' + H_2O = R.CO.CH_2.R'$$

and

$$\underset{R'}{\overset{R}{\diagdown}}C : C : C\underset{R'''}{\overset{R''}{\diagup}} + H_2O = \underset{R'}{\overset{R}{\diagdown}}CH.CO.CH\underset{R'''}{\overset{R''}{\diagup}}$$
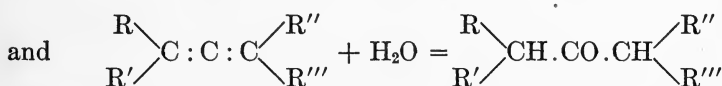
With *sulphuric acid,* the reaction is carried out by dissolving the hydrocarbon in the cold concentrated acid and pouring this solution immediately on to ice.[8]

The mechanism appears to be the formation of an unstable sulphuric acid derivative which decomposes on contact with water to form an unsaturated alcohol which immediately isomerizes into the ketone. Thus with ethyl-acetylene, we should have successively:

$$CH_3.CH_2.C \vdots CH + H_2SO_4 = CH_3.CH_2C\underset{O.SO_3H}{\overset{CH_2}{\diagup}}$$

$$CH_3.CH_2.C\underset{O.SO_3H}{\overset{CH_2}{\diagup}} = H_2SO_4 + CH_3.CH_2.C(OH) : CH_2$$

$$CH_3.CH_2C(OH) : CH_2 = CH_3.CH_2.CO.CH_3.$$
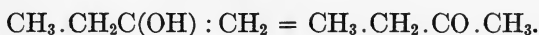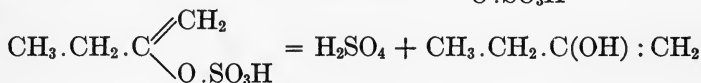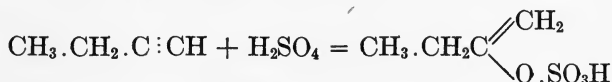
In the case of *true acetylene hydrocarbons,* the product is a *methyl ketone.* With *disubstituted acetylenes,* two isomeric ketones are obtained. This is the case with *methylamylacetylene.*[9]

[4] Brooks and Humphrey, *Ibid.,* **40,** 822 (1918).

[5] Saytzeff, *J. prakt. Chem.* (2), **37,** 284 (1888).

[6] Wiggers, *Annalen,* **57,** 247 (1846).

[7] Würtz, *Bull. Soc. Chim.* (2), **42,** 286 (1884).

[8] Béhal, *Bull. Soc. Chim.* (2), **47,** 33 (1887).

[9] Béhal, *Ibid.* (2), **50,** 359 (1888).

Acetylene should give *acetaldehyde,* but this condenses with loss of water (795) and *crotonic aldehyde* is the chief product.[10]

309. Water solutions of *mercuric salts,* the chloride, bromide, and sulphate, cause the same formation of ketones in consequence of the temporary production of combinations of the hydrocarbon and the salt, which are then decomposed by water. Thus *allylene,* CH_3.-$C:CH$, gives *acetone,* $CH_3 . CO . CH_3$.

Acetylene behaves normally, yielding *acetaldehyde:* [11]

$$CH:CH + H_2O = CH_3.CHO.$$

Acetylene is absorbed at 25 to 45° in a solution of mercuric oxide in water containing 45% or less sulphuric acid, or 25% phosphoric acid. The solution saturated with the gas is warmed to 80 to 100° when acetaldehyde is given off. The solution is then cooled and made to take up more gas and so on. By a number of repetitions the mercuric salt produces 20 times its own weight of acetaldehyde.[12] A stronger solution of sulphuric acid is unfavorable as it would cause the formation of crotonic aldehyde and other condensation products. (See the direct formation of *acetic acid* (261).)

310. This hydration of acetylene to acetaldehyde can likewise be accomplished by passing the moist gas over zinc, nickel, or ferrous oxides at 300°. There is the formation of a certain amount of acetaldehyde and also of crotonic aldehyde. If the moist acetylene contains ammonia, the formation of acetaldehyde is shown by the deposit of crystals of *aldehyde ammonia.*[13]

311. **Nitriles.** *Nitriles* dissolved by gentle warming in *sulphuric acid* diluted with 20% of water, are transformed into *amides.* The same transformation can be effected also by caustic soda and potash; but, especially if the operation is carried on in alcohol solution in the neighborhood of 100°, the hydration may go so far as to break the amide down into ammonia and the acid, which is at least partially neutralized by the alkali.

312. **Imides.** It is the same way with *imides, succinimide,*
CH_2-CO
— $\big\rangle NH$, warmed with a small amount of baryta water, gives
CH_2-CO
at first *amido-succinic acid,* $H_2N . CO . CH_2 . CH_2 . CO_2H$,[14] the further hydration of which yields *succinic acid.*

[10] BERTHELOT, *Compt. rend.,* **128**, 336 (1899).

[11] KUTSCHEROFF, *Berichte,* **17**, 13 (1884).

[12] DREYFUS, *French patent,* 487,411 (1918).

[13] CHICHIBABINE, *J. Russian Phys. Chem. Soc.,* **47**, 703 (1915); *C. A.,* **9**, 2512 (1915).

[14] TEUCHERT, *Annalen,* **134**, 136 (1865).

Likewise aspartic imide, $\begin{array}{c} H_2N.CH-CO \\ | \\ CH_2-CO \end{array} \Big\rangle NH$, heated to 100° with

aqueous *ammonia,* adds a molecule of water to give *asparagine,* $HOOC.CH_2.CH(NH_2).CONH_2$.[15]

Acetaldehyde in water solution causes cyanogen to add two molecules of water to form *oxamide,* $H_2N.CO.CO.NH_2$.[16]

II. — Hydrations with Decomposition

313. A hydration which results in the decomposition of the molecule is usually called *hydrolysis.*

§ 1. HYDROLYSIS IN WATER SOLUTION

Hydrolysis of Esters. The hydrolysis of esters is known as *saponification.*

When a water solution of methyl acetate or ethyl acetate is kept in the cold, there is a slow decomposition by water to give the alcohol and free acid:

$$CH_3.CO_2.C_2H_5 + H_2O = CH_3.CO_2H + C_2H_5.OH$$
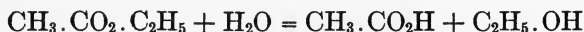
The reverse reaction of esterification tends to reform the ester so the decomposition is never complete; the reaction tends to an equilibrium, the more water there is present, the more ester will be decomposed, but this limit is not reached at ordinary temperatures till after some years. In several days, the amount of ester decomposed is only about 1%. On the contrary, if a small amount of hydrochloric acid, or other strong acid, be added to the mixture, the reaction becomes very rapid, the limit being reached in 24 hours.

Furthermore, the acid added is in no way changed. It is entirely precipitated by silver nitrate which shows that it has not formed an appreciable amount of ethyl chloride. Up to a certain limit, the saponifying power of the acid is proportional to its concentration; and for different acids, at the same molecular concentrations, the saponifying power is proportional to the strength of the acid which is measured by its electrolytic dissociation, and consequently this activity is defined by the number of hydrogen *ions* in a unit volume of the solution. Hydriodic, hydrobromic, nitric and chloric acids, which are strongly ionized, are consequently powerful catalysts, and so is *sulphuric acid* which is most commonly used for this purpose.

[15] KOERNER and MENOZZI, *Gaz. Chim. Ital.,* **17**, 173 (1887).
[16] LIEBIG, *Annalen,* **113**, 246 (1860).

314. This action is general and applies equally well to the saponification of fats which are esters of glycerine with the fatty acids. A fat heated with water and 4% sulphuric acid to 120° is completely hydrolyzed in 12 hours, 42% of the fatty acids being liberated in the first hour. To produce a like decomposition with water alone requires heating to 220° in an autoclave.[17]

315. In very dilute solutions the velocity of saponification is the same with hydrochloric, hydrobromic, hydriodic, nitric, chloric and methyl sulphuric acids of the same acidity and is proportional to the concentration of the acid.

It is the same for all the esters of a given organic acid with different primary alcohols.[18]

316. On the other hand, the velocity changes greatly when the organic acid from which the ester is derived is changed. Thus for ethyl esters the saponification velocity of the *formate* is 25 times that of the *acetate,* 50 times that of the *isobutyrate,* 100 times that of the *valerate,* and 4,000 times that of the *benzoate.*

317. The presence of neutral metallic salts modifies the velocity, chlorides accelerating the saponification by hydrochloric acid,[19] while sulphates retard the action of sulphuric acid.

Pressure may also have an effect; in the case of the saponification of methyl acetate by hydrochloric acid, pressure increases the velocity.

318. The soluble bases, potassium, sodium, barium, and calcium hydroxides have an analogous effect which, at first sight, would be attributed to the affinity of the base for the acid liberated, were the amount of ester saponified not disproportionate to the amount of base reacting. The real reason for the saponification is again found in the dissociation of the bases in dilute solution into ions.

The saponification of fats has given clear evidence on this point. The amount of lime required to saturate all of the fatty acids of a fat is about 9.7%, and in practice might reach 12 to 14%, but experience shows that 1% is sufficient for complete saponification in water at 190° under 12 atmospheres pressure, while 3% produces this result in 8 to 10 hours, at 170° and 8 atmospheres.[20]

It appears from the above figures that, in spite of the additional energy liberated by the combination of the bases with the acids, the catalytic activity of the bases is less than that of the strong acids.

[17] LEWKOWITSCH, *Conftér. à la Soc. Chim.,* 1909, 12.

[18] LÖWENHERZ, *Z. phys. Chem.,* **15**, 395 (1894).

[19] TREY, *J. prakt. Chem.* (2), **34**, 353 (1886). EULER, *Z. phys. Chem.,* **32**, 348 (1900).

[20] LEWKOWITSCH, *loc. cit.,* p. 8.

319. For different strong bases, in very dilute solution and at the same concentration, the saponification velocity is independent of the nature of the base, whether it be potassium, sodium, barium or calcium hydroxide, but is proportional to the concentration of the base.

For esters derived from the same acid, the velocity changes greatly with the alcohol, thus *methyl acetate* is saponified twice as rapidly by caustic soda in the cold as is *isobutyl acetate*.[21] The influence of the nature of the acid is less than it is in saponification by strong acids. Thus when methyl esters are saponified by caustic soda at 14°, the velocity for the acetate is about double that for the isobutyrate, six times that for the isovalerate, and quadruple that for the benzoate.

In the saponification of ethyl acetate by bases, the presence of neutral salts cuts down the velocity.[21]

320. The saponification of chlorine derivatives is not usually possible, but benzal chloride and benzotrichloride are hydrolyzed to benzaldehyde and benzoic acid by water alone when heated under pressure.

The saponification of benzal chloride, $C_6H_5CHCl_2$, by water alone requires a temperature of 140–160°.[22] In the factory it is usually effected by means of milk of lime. In the presence of *iron powder,* the reaction can be carried out at 90–95°.[23]

It is the same way with *benzotrichloride* which is readily transformed into benzoic acid in the presence of *iron, ferric chloride, oxide* or *benzoate*.[23]

321. **Ethers.** Water alone breaks up ethers into two molecules of the alcohols very slowly.[24] The addition of small quantities of sulphuric acid greatly accelerates the reaction.[25]

322. **Acetals.** Acetals can be regarded as mixed ethers derived from alcohols and the unstable gylcols of which aldehydes and ketones are the anhydrides. Their hydrolysis cannot be accomplished by water alone, nor by alkalies, even when hot. On the contrary, it is easily effected by boiling with either dilute *hydrochloric acid* or with *sulphuric acid* diluted with four volumes of water, the aldehyde and the alcohol being set free.

323. **Polysaccharides.** *Polyoses* and polysaccharides such as sucrose, lactose, maltose, trehalose and even starch, dextrine and

[21] ARRHENIUS, *Z. phys. Chem.,* **1**, 110 (1887).

[22] LIMPRICHT, *Annalen,* **139**, 319 (1866).

[23] SCHULTZE, *German patent,* 82,927.

[24] LIEBEN, *Annalen,* **165**, 136 (1873).

[25] ERLENMEYER, *Zeit. f. Chemie,* **4**, 343 (1868).

cellulose can be regarded as ethers or acetals involving the many alcohol groups and the aldehyde or ketone groups of the simple hexoses. Their hydrolysis into the simple sugars can be realized more or less readily by the aid of small quantities of acids as catalysts.

324. The *inversion* of cane sugar, that is, its complete hydrolysis into glucose and fructose, can be brought about by traces of mineral acids and is, perhaps, the earliest catalytic reaction to be observed.[26] *Hydrochloric, sulphuric,* or even *oxalic acid* can be used and the velocity of the hydrolysis is proportional to the concentration of the hydrogen *ions* resulting from the electrolytic dissociation of the acid. Concentrated sugar solutions are rapidly inverted by traces of acid. A solution containing 80 g. sugar to 20 g. water, with the addition of 0.004 g. hydrochloric acid, is completely inverted by boiling for an hour.[27] Even *carbonic acid* can cause this reaction, slowly in the cold, rapidly when heated. A sugar solution saturated with carbon dioxide and heated for an hour in a sealed tube is completely inverted.[28]

The velocity of the inversion of sugar by strong acids is increased by the addition of neutral salts.[29]

When the reaction is carried on in alcohol solution, the velocity varies considerably with the proportion and nature of the solvent.[30] Increase in the concentration of the sugar increases the velocity.[31]

High pressure diminishes the velocity of inversion by hydrochloric acid, the diminution being about 1% for 100 atmospheres.[32]

325. The hydrolysis of *maltose* is slower than that of cane sugar, requiring at least three hours of boiling with 3% sulphuric acid.[33]

Trehalose is slowly hydrolyzed into glucose by warming with dilute sulphuric acid.[34]

326. *Sulphuric acid* diluted with 33 parts of water is used in the commercial preparation of glucose by the hydrolysis of starch at 100° for three hours. The addition of a little *nitric acid* to the sul-

[26] CLEMENT and DESORMES, *Ann. Chim. Phys.,* **59**, 329 (1806).

[27] WOHL, *Berichte,* **23**, 2086 (1890).

[28] LIPPMANN, *Berichte,* **13**, 1823 (1880).

[29] SPOHR, *Z. physik. Chem.,* **2**, 194 (1888). ARRHENIUS, *Ibid.,* **4**, 226 (1889). EULER, *Ibid.,* **32**, 348 (1900).

[30] BURROWS, *J. Chem. Soc.,* **105**, 1260 (1914).

[31] ROSANOFF and POTTER, *J. Amer. Chem. Soc.,* **35**, 248 (1913).

[32] RÖNTGEN, *Wiedermann's Annalen* (3), **45**, 98 (1892). ROTHMUND, *Z. physik. Chem.,* **20**, 170 (1896).

[33] MEISSL, *J. prakt. Chem.* (2), **25**, 120 (1882).

[34] MÜNTZ, *Jahresber.,* **1873**, 829. BERTHELOT, *Ann. Chim. Phys.* (3), **55**, 272 (1859).

phuric acid seems to shorten the time required. There is an intermediate formation of *dextrine* which is, in turn, hydrolyzed by the dilute acid.

327. Glucosides. The various substances designated by this name are numerous among vegetable products and have a constitution analogous to that of the polysaccharides. Their hydrolysis by pure water can usually be accomplished only by heating to high temperatures in sealed tubes, but by boiling with *dilute mineral acids*, they are decomposed into a sugar (usually glucose) and one or more substances of various kinds.

The action of acids is comparable to that of soluble ferments, such as *emulsine*, but is more rapid and more drastic, the product of hydrolysis being sometimes altered by the peculiar action of the acid.

328. Thus *arbutine* when boiled with dilute *sulphuric acid* is hydrolyzed into 1 molecule of glucose and 1 molecule of hydroquinone,[35] which is identical with the results obtained by long contact with emulsine in the cold.

Helicine is hydrolyzed by dilute acids into glucose and *salicylic aldehyde*,[36] and *quercitrine* into *isodulcite* and *quercitine* (tetrahydroxyflavanol.[37]

The *ruberythric* acid of madder root gives *alizarine* and 2 molecules of glucose when boiled with dilute acids.[38]

329. *Salicine* heated to 80° with 10 parts of fuming hydrochloric acid (d. 1.25), gives 2 molecules of glucose[39] and *saliretine*, $O(C_6H_4 . CH_2 . OH)_2$, while the action of emulsine in the cold or boiling with dilute acid leads to *saligenine*, $o.HO . C_6H_4 . CH_2OH$.[40]

Amygdaline is decomposed by boiling with dilute hydrochloric or sulphuric acid, just as it is in the cold by emulsine, into benzaldehyde, hydrocyanic acid, and 2 molecules of glucose:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5 . CHO + HCN + 2C_6H_{12}O_6.$$
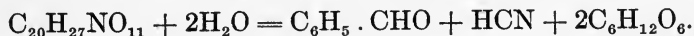
But when acids are used the hydrocyanic acid formed is rapidly hydrolyzed into formic acid and ammonia.[41]

Coniferine is split by emulsine into glucose and *coniferyl alcohol*, but when the hydrolysis is carried out by boiling with dilute acids, the alcohol is resinified.[42]

[35] KAWALIER, *Annalen*, **84**, 356 (1852).
[36] PIRIA, *Annalen*, **56**, 64 (1845).
[37] RIGAUD, *Annalen*, **90**, 289 (1856).
[38] GRAEBE and LIEBERMANN, *Annalen, Supl.*, **7**, 296 (1870).
[39] KRAUT, *Annalen*, **156**, 124 (1870).
[40] PIRIA, *Annalen*, **56**, 37 (1845).
[41] LUDWIG, *Jahresber.*, **1855**, 699 and **1856**, 679, *Arch. Pharm.* (2), **87**, 273.
[42] TIEMANN *and* HAARMANN, *Berichte*, **7**, 611 (1874).

330. The dilute acids can be replaced by dilute *soluble bases* such as sodium, potassium and barium hydroxides or even by a solution of *zinc chloride* (for example with *helleborine*).[43]

331. Acidamides and Analogous Compounds. The derivatives formed by the loss of a molecule of water between an organic acid and ammonia, an amine, hydroxylamine, hydrazine, phenylhydrazine or semicarbazid can be more or less readily hydrolyzed into the molecules from which they were derived. This hydrolysis can be accomplished by mineral acids which combine with the ammonia or other base or by aqueous alkalies which unite with the organic acid.

Amides which can be hydrolyzed by boiling with pure water are much more rapidly hydrolyzed by heating with dilute mineral acids or with dilute alkalies.

332. The hydrolysis of *oximes* takes place on contact with hot concentrated hydrochloric acid, which combines with the hydroxylamine that is liberated along with the aldehyde or ketone.

Phenylhydrazones are hydrolyzed in the cold with concentrated hydrochloric acid which combines with the phenylhydrazine.

Bisdiazoacetic acid, $HOOC.C\begin{smallmatrix}N{-}{-}{-}N\\ \\NH{-}NH\end{smallmatrix}C.COOH$, is hydrolyzed

by sulphuric acid diluted with 4 molecules of water to give 2 molecules of hydrazine and 2 molecules of oxalic acid.[44]

333. Heating in a sealed tube with a concentrated solution of hydrochloric acid causes the hydrolysis of *sulphocyanic esters:*

$$CN.SR + 2H_2O = R.SH + CO_2 + NH_3,$$

as well as of *mustard oils,* or *isosulphocyanic esters:*

$$CS:NR + 2H_2O = H_2S + CO_2 + \underline{H_2NR}.$$
$$\text{amine}$$
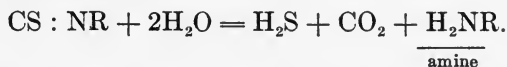
334. On the contrary, the hydrolysis of *isocyanic esters,* or *alkyl carbylamines,* is carried out by boiling with aqueous [45] or alcoholic [46] potash:

$$CO:NR + H_2O = CO_2 + H_2NR,$$
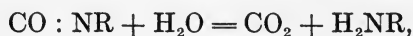
and the activity of the base can be attributed to its affinity for carbonic acid.

[43] Husemann and Marmé, *Annalen,* **135**, 55 (1865).
[44] Curtius and Lang, *J. prakt. Chem.* (2), **38**, 532 (1888).
[45] Wurtz, *Ann. Chim. Phys.* (3), **42**, 43 (1854).
[46] Haller, *Bull. Soc. Chim.* (2), **45**, 706 (1886).

335. The hydrolysis of *amides* and of *alkyl amides* can be carried out by acids or alkalies indifferently. In the case of aliphatic amides, the reaction is usually effected by heating with alcoholic potash or soda and takes place slowly, sometimes requiring heating for several days. We have:

$$R . CO . NH_2 + H_2O = R . CO_2H + NH_3,$$
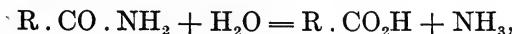
and we may believe that the affinity of the potash for the acid determines the reaction.

336. In most of the above reactions the catalytic rôle of the acids and bases does not appear, at first sight, to be well established. We can, however, assume that it is really catalytic, since in the reactions that have been most closely studied, such as the hydrolysis of *amides*, amounts of acid far less than equivalent to the amides greatly accelerate the reaction. In the case of the hydrolysis of *acetamide* by dilute mineral acids, it has been found that the activity of the acids is proportional to their ionization and to the concentration of the ions in the system.[47]

§ 2. — HYDROLYSIS IN GASEOUS SYSTEMS

337. **The Saponification of Esters.** *Titania*, TiO_2, which readily causes the esterification of alcohols by aliphatic acids (767), between 280 and 300°, just as readily reverses the reaction and brings about the saponification of esters by water. The rapid passage of a mixture of water and ester vapors in equivalent amounts over the oxide at 280 to 300° is sufficient to reach about 30% hydrolysis and this percentage is increased as the relative amount of water is increased till practically complete hydrolysis is effected by very large amounts of water.

Thoria can produce the same effect but with less activity.[48]

338. **Ethers.** *Thoria*, ThO_2, which effectively catalyzes the formation of phenyl oxide, $(C_6H_5)_2O$, from phenol at 400 to 500°, can equally well decompose it when phenyl ether and water vapor are passed over the heated oxide, the decomposition reaching 50%.[49]

339. **Hydrolysis of Carbon Disulphide.** The reaction of water vapor on *carbon disulphide* in the presence of appropriate catalysts, such as *ferric oxide,* can be considered a case of hydrolysis. The reaction is incomplete but goes in this direction:

$$CS_2 + 2H_2O = CO_2 + 2H_2S.$$

[47] OSTWALD, *J. prakt. Chem.* (2), **27**, 1 (1883).
[48] SABATIER and MAILHE, *Compt. rend.,* **152**, 494 (1911).
[49] SABATIER and ESPIL, *Bull. Soc. Chim.* (4), **15**, 228 (1914).

This reaction applied to illuminating gas suppresses 67% of the carbon disulphide which it contains and, if the hydrogen sulphide is absorbed as rapidly as it is formed, all of the carbon disulphide is eliminated.[50]

III. — ALCOHOLYSIS

340. The action of alcohols on esters can be compared to the saponification of esters by water and is likewise catalyzed by small quantities of strong mineral acids, *hydrochloric* and *sulphuric*.[51]

If a primary aliphatic alcohol, R'OH, is mixed with the ester derived from an acid, RCOOH and a complex alcohol, MOH, we shall have: [52]

$$R . CO . OM + R' . OH = MOH + R . CO . OR'.$$
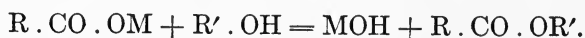
The alcohol, MOH, is set free. This is what takes place when *methyl, ethyl, propyl alcohols* and the like attack the esters of *borneol, glycerine*, etc., in the presence of a minute amount of hydrochloric acid.

Thus *bornyl acetate* in a *methyl alcohol* solution, containing 1% hydrochloric acid, is rapidly decomposed into *borneol* and *methyl acetate.*

Glycerides dissolved in *absolute alcohol* containing a few per cent of *hydrogen chloride* yield glycerine and the fatty acid ethyl esters.[53]

341. Haller has designated these saponifications which take place readily with all the fats, by the name of *alcoholysis*. They can be carried out by mixing 100 g. of a fat with 200 g. dry *methyl alcohol* containing 1 or 2 g. hydrogen chloride and heating on a steam bath under reflux till the mixture becomes homogeneous. If necessary

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[50] GRILLET, *Soc. Tech. de l'Ind. du gaz en France,* 1918, 245.

[51] Sodium alcoholate is an even better catalyst than hydrochloric acid. In the transformation of methyl benzoate into the ethyl ester, sodium ethylate was found to be about 4,000 times as efficient as an equivalent amount of hydrochloric acid. (REID, *Amer. Chem. J.,* 45, 506 (1911)). — E. E. R.

[52] This reaction is a perfectly general one and simple alcohols may be replaced as well as " complex," thus methyl alcohol replaces ethyl and vice versa as shown by REID (*Amer. Chem. J.,* 45, 479 (1911)), and recently by REIMER and DOWNES (*J. Amer. Chem. Soc.,* 43, 945 (1921)).

For a number of references on alcoholysis see article by PARDEE and REID (*J. Ind. and Eng. Chem.,* 12, 129 (1920)). It is a reversible reaction, the equilibrium point depending on the concentrations and activities of the two alcohols competing for the acid and hence can never be complete, no matter how much one alcohol predominates. — E. E. R.

[53] ROCHLEDER, *Annalen,* 59, 260 (1846). BERTHELOT, *Ann. Chim. Phys.* (3), 41, 311 (1854).

more hydrogen chloride may be added during the reaction.   The mixture is finally poured into brine which dissolves the glycerine and causes the methyl esters of the fatty acids to separate as a top layer.[54]

This reaction is rapid with *cocoa butter* [55] and *castor oil*, with which heating for several hours is sufficient,[56] and is slower with drying oils such as *linseed*.[57]   It goes just as well with *ethyl, propyl,* and *isobutyl* alcohols.[56]

[54] HALLER, *Compt. rend.,* **143,** 657 (1906).
[55] HALLER and YOUSSOUFFIAN, *Compt. rend.,* **143,** 803 (1906).
[56] HALLER, *Compt. rend.,* **144,** 462 (1907).
[57] HALLER, *Compt. rend.,* **146,** 259 (1908).

CHAPTER VIII

HYDROGENATIONS

HYDROGENATIONS IN GASEOUS SYSTEM, GENERALITIES, USE OF NICKEL

342. Historical. The catalytic properties of finely divided platinum discovered by Davy and Doebereiner at the beginning of the nineteenth century, have shown its power to cause oxidations. Several chemists attempted to apply the special powers of platinum sponge to other reactions and particularly to the direct addition of hydrogen to various substances. In 1838, Kuhlmann showed that nitric oxide, or the vapors of nitric acid, warmed with hydrogen in the presence of platinum sponge gave ammonia.[1] In 1852, Corenwinder observed that the same agent caused hydrogen to combine *rapidly*, though incompletely, with iodine between 300 and 400°.[2] In 1863, Debus, with the aid of platinum black, accomplished the addition of hydrogen to hydrocyanic acid to form methyl amine,[3] and found that ethyl nitrite is transformed into alcohol and ammonia under the same circumstances. In 1874, von Wilde succeeded in transforming acetylene into ethylene and then into ethane, by platinum black at room temperature.[4]

343. In a series of investigations continued since 1897, Sabatier and Senderens (1897–1905), then Sabatier and Mailhe (1904–1908), and Sabatier and Murat (1912–1914) have established and extended to a large number of cases a general method of direct hydrogenation of volatile organic compounds, based on the use of finely divided catalytic metals and particularly on the use of nickel recently reduced from the oxide.[5]

[1] KUHLMANN, *Compt. rend.*, **7**, 1107 (1838).

[2] CORENWINDER, *Ann. Chim. Phys.* (3), **34**, 77 (1852).

[3] DEBUS, *Annalen*, **128**, 200 (1863).

[4] VON WILDE, *Berichte*, **7**, 352, (1874).

[5] These investigations have been published in a large number of original articles of which more than 50 are in the Comptes Rendus de l'Academie des Sciences as well as in various collective memoirs of which the chief are: SABATIER, *Vth Congress of Pure and Applied Chemistry*, Berlin, 1904, IV, 663. SABATIER and SENDERENS, *Confer. Soc. Chim.*, Paris, 1905. SABATIER, *Rev. Gen. Sc.*, **16**, 842 (1905). SABATIER, *Rev. Gle. Chim.*, **8**, 381 (1905). SABATIER and SENDERENS,

As early as 1902 this new method was taken up in many French and foreign laboratories and numerous chemists have contributed, along with the above authors, to widen its application.

344. Essentially the process consists in passing the vapors of the substance mixed with hydrogen over a layer of the catalytic metal, *platinum black,* or even *nickel, cobalt, iron,* or *copper* reduced from the oxides in the same tube in which the hydrogenation is to be carried on, maintained at a suitable temperature, sometimes room temperature but more commonly somewhere between 150 and 200°. A temperature around 180° is very frequently found to be the most suitable.

Of the five metals mentioned above, nickel is the most active and it and cobalt are the only ones capable of effecting certain hydrogenations such as that of the benzene nucleus. Copper is less powerful and platinum and iron are between cobalt and copper.

345. The apparatus employed by Sabatier and his co-workers comprises:

1. A hydrogen generator.

2. A working tube to contain the catalytic metal.

3. An arrangement for introducing the vapors to be hydrogenated along with the hydrogen.

4. A receiver to collect the product of the reaction.

346. **The Hydrogen Generator.** The hydrogen can be prepared by the action of commercial hydrochloric acid diluted with half its volume of water on ordinary granulated zinc. The continuous generator of Sainte-Clair Deville consists of two large flasks of 10 to 15 l. of which the lower tubulures are connected by large rubber tubing. One flask is filled with granulated zinc and the other with hydrochloric acid. The gas is washed with strong caustic soda and then with concentrated sulphuric acid. A graduated safety tube in the acid wash bottle serves to indicate the gas pressure. Between the two wash bottles is a stop cock to regulate the gas and beyond the acid wash bottle is a pinch cock for further adjustment of the pressure. To secure a regular delivery of the gas it is sufficient to maintain the acid in the safety tube at a constant height. On account of

Ann. Chim. Phys. (8), **4**, 319 (1905). SABATIER, *VIth. Congress Pure and Appl. Chem.,* Rome, 1906, Xth. *Sect.* 174. SABATIER and MAILHE, *Ann. Chim. Phys.* (8), 16, 70 (1909). SABATIER, *Berichte,* **44,** 1984 (1911). SABATIER, Address at Stockholm on the reception of the Nobel Prize, *Rev. Scient.,* **1**, 289 (1913). SABATIER, Confer. à Toulouse au Congrès du gaz, *Le Gaz,* **57,** 1914. SABATIER, Confér. à University of London, *Rev. Gle. Chim.,* **17**, 185 and 221 (1914). SABATIER and MURAT, *Ann. de Chim.* (9), **4,** 253 (1915).

the large dimensions of the apparatus, a constant evolution of gas can be maintained for at least six hours.

The hydrogen must be carefully freed from impurities derived from the zinc or from the acid (hydrogen sulphide, arsine, phosphine and hydrochloric acid vapors). For this purpose it passes through a tube of Jean glass, filled with copper turnings kept at a dull red, which stops the major part of the impurities. The purification is completed by passing the gas through a long tube filled with slightly moist fragments of caustic potash which retains acid vapors as well as any remaining hydrogen sulphide. The purified gas passes to the reaction tube.

The complete drying of the gas appears superfluous as it has been shown that moist hydrogen hydrogenates benzene or phenol, over nickel, at least as well as dry.[6]

Electrolytic hydrogen, which is on the market in steel cylinders at high pressures, can be used to advantage. These cylinders fitted with suitable reducing valves, furnish a nearly pure gas which can be freed from the small amount of oxygen which it contains by passing over red hot copper in a tube followed by a drying tube containing caustic potash.

347. The Reaction Tube. In a glass tube 65 to 100 cm. long and 14 to 18 mm. inside diameter, a longer or shorter (35 to 80 cm.) thin layer of platinum black or of the oxide, from which the catalytic metal is to be prepared, is spread. The tube is heated in a gas furnace such as is used for organic combustions but in which the burners have wing tips with little holes so that there are a large number of little flames equal in size and close together distributing the heat evenly.

The tube is laid in a semicircular trough and rests on a rather thick layer of calcined magnesia or fine sand. The temperature is taken simply with a glass thermometer graduated to 450° which is embedded in the trough by the side of the tube and which may be moved from place to place to test the evenness of the heating.

The temperature read on the thermometer is always a little lower than that in the tube, the difference being greater at higher temperatures.[7] For temperatures around 180 to 200° the difference is hardly more than 10 to 15°, while at 350° it may be as great as 35°. The limits between which the reactions go on are usually wide enough so that this approximate determination of the temperature is sufficient.

[6] Sabatier and Espil, *Bull. Soc. Chim.* (4), **15**, 228 (1914).
[7] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **20**, 296 (1910).

348. If more exact determinations are desired a rectangular copper oven 12 x 15 x 65 cm. down the centre of which runs a copper tube is used. The thermometer and the tube containing the previously prepared catalysts are placed in this tube side by side. A metallic regulator contained in a copper tube parallel to the first controls the gas and maintains the temperature at which it is set. The copper box is filled with a liquid which up to 270° may be boiled linseed oil, or for higher temperatures a mixture of equal weights of sodium and potassium nitrates which is liquid above 225°. For delicate hydrogenations with such substances as benzoic esters, Sabatier and Murat have employed a massive bronze block, 65 cm. long, 10 cm. wide and 7 cm. high, of rectangular cross section, with rounded corners. Two symmetrically placed holes 25 mm. in diameter run from one end to the other of the block: the one contains the tube carrying the nickel and the other the metallic regulator which controls the gas supply of the furnace. Any desired temperature is thus obtained very uniformly on account of the large mass of the good conducting metal. On account of this conductivity, the temperature may be raised quickly. Small holes parallel to the large ones receive the thermometers.

The temperature may be first carried to 350° for the preparation of the nickel and then lowered to any desired temperature, such as 180°, for carrying out the hydrogenation.

In case nickel-coated pumice is used as catalyst (126) a very useful arrangement is to fill the two limbs of a vertical U-tube with the catalyst. This tube may be heated in an air bath to 350° for reducing the nickel and then lowered into an oil bath kept at 180° or into the vapors of boiling aniline, 185°, for the hydrogenation.

Heating on the furnace is less regular and requires close attention but has the advantage that the interior of the tube may be watched.

349. Heating by electric resistance may be conveniently employed. The reaction tube is surrounded by asbestos paper on which is wound a 1 mm. ferro-nickel spiral which, in turn, is surrounded by a second layer of asbestos paper. By the aid of suitable resistances the current is regulated to show the proper readings on an ammeter. The temperatures in the centre of the tube corresponding to various ammeter readings are previously determined by experiment.[8]

This method of heating has the advantage, as compared to the open furnace, that the tube is heated uniformly around its whole

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[8] The conditions of the experiment must be exactly duplicated during the calibration since otherwise incorrect estimates of temperatures are possible as varying amounts of heat are removed by varying currents of gas through the tube. — E. E. R.

circumference, and, with it it is best to employ nickeled pumice filling the whole tube rather than a layer of nickel resting in the bottom.[9]

350. Introduction of the Substance. The method of introducing the substance to be hydrogenated varies, of course, according to its physical state.

If it is a *gas* the forward end of the tube containing the catalyst carries a two-hole stopper with two tubes, one for the gas and one for the hydrogen. The gas is furnished by a continuous generator (as with acetylene or carbon dioxide) or by a metal or glass gasometer into which it is measured in advance (carbon monoxide, propylene, nitrous oxide), or even by a discontinuous apparatus which can be operated sufficiently regularly (as for ethylene, or nitric oxide). A wash cylinder with pressure indicator interposed between a stop cock and a screw pinch cock as has been described above for hydrogen (346), serves to admit the gas at any desired constant rate. In the case of discontinuous generators, a safety valve is arranged by having a side outlet tube dipping under mercury so that the excess of gas may escape.
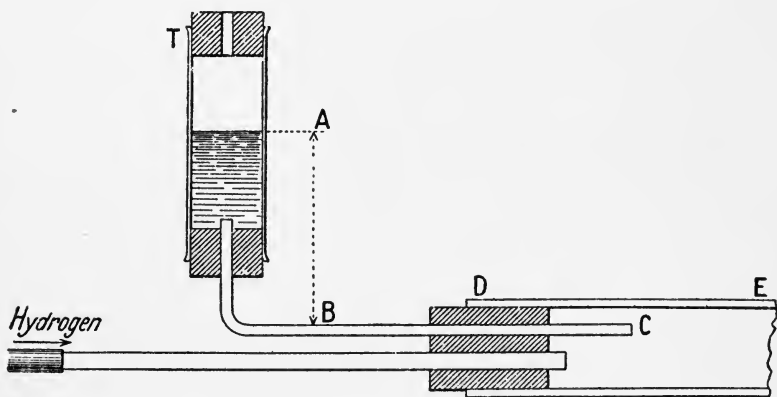
351. For most *liquids*, Sabatier and Senderens have devised an extremely simple apparatus. The liquid is conducted by a capillary tube to the interior of the reaction tube. The liquid is placed in a large vertical tube T, the lower end of which carries a stopper through which passes the vertical portion of a bent capillary tube, the horizontal portion of which passes through the stopper in the end of the reaction tube.

For a given liquid, the flow is more rapid the larger the bore of the

[9] Brunel, *Ann. Chim. Phys.* (8), **6**, 205 (1905).

capillary tube and the greater the head of liquid, AB. By maintaining this head constant, a regular flow of liquid is obtained.

It is well to arrange it so that the liquid does not fall from the end of the capillary tube in drops, but flows steadily from its end either on to the wall of the reaction tube or over the surface of the cork in its end.

The selection of the capillary tube depends on the viscosity of the liquid, a smaller tube being used for mobile liquids.

It is evident that there are two independent ways of regulating the flow of the liquid, by changing the diameter of the capillary tube or altering its height. Besides, the capillary tube can be fed by a reservoir with as large a surface as may be desired and, for experiments of long duration, the tube A can be placed in communication with a flask of large size in which the variations of level are very slow.

It is convenient for the stopper D to be at some distance from the heated portion of the tube; 3 to 4 cm. is sufficient. The layer of metal should not commence for a little distance, about 10 cm. from the stopper. The liquid introduced by the capillary volatilizes regularly in this open space. It is important to watch that the liquid does not wet the catalyst which is frequently altered by contact with the liquid.

352. We may also operate by bubbling the hydrogen through the liquid to be hydrogenated, thus carrying along the vapors. If the liquid is very volatile (acetaldehyde, propionic aldehyde, nitrogen peroxide, etc.) cooling is necessary so that the amount of the vapors carried along will not be too great.

If the liquid is only slightly volatile, heating may be required, always selecting a temperature so that the hydrogen will be in excess of that required for complete hydrogenation.[9a]

353. For *solid* substances which melt below 100°, the same appa-

[9a] In order to get an equimolecular mixture of the vapor and hydrogen, the liquid through which the hydrogen is bubbled must be kept at such a temperature that its vapor pressure is 380 mm. For some liquids this temperature may be found from tables in the literature. The vapor pressure curves for various classes of liquids are not quite similar, owing to different degrees of association, but for most organic liquids, except the lower alcohols, the vapor pressure is 380 mm. at from 20 to 24° below their boiling points. To have a little more than 1 molecule of hydrogen to 1 of the vapor the liquid should be kept at from 25 to 30° below its boiling point. These same liquids have vapor pressures approximately one third of an atmosphere at 32 to 36° below their boiling points and should be kept at such temperatures to obtain 2 molecules of hydrogen to 1 of the vapor or at somewhat lower temperatures if an excess of hydrogen is desired, as is usually the case. Similar calculations may be made when a larger number of molecules of hydrogen to one of the compound are desired. — E. E. R.

ratus may be used by surrounding the capillary tube and the vertical tube T with a sort of cylindrical air bath, the lower end of which is heated by a Bunsen burner. The current of warm air is sufficient to maintain the substance in the liquid condition. This method may be used with phenol, the cresoles, the nitronaphthalines and naphthaline.

A thick copper capillary tube brazed on to a copper vertical tube T may be used, and this may be heated directly by a small flame.

When the substance melts above 100°, it is placed in long porcelain boats in the forward part of the tube, a long tube being selected. The volatilization of the substance is effected by careful heating, a portion at a time, starting from the end next to the heated metal. The reaction is of course limited to the amount of material in the boats and is consequently intermittent.

Solids melting below 180° may be kept fused by a suitable air bath and the vapors carried on by the hydrogen which is bubbled through.

354. When the product of the hydrogenation is a liquid, it is frequently sufficient to mix some of it with the solid to be hydrogenated, thus lowering the melting point so that the usual apparatus for liquids may be employed. This is the case with phenol and with ortho and meta cresoles.

The use of solvents which can not be hydrogenated, such as water, paraffine hydrocarbons (hexane, heptane, etc.) usually gives poor results, particularly when water is used.

355. **Apparatus for Collecting the Reaction Products.** If the products of the hydrogenation are all gases, they are collected at the end of the catalyst tube in a gas holder over water, care being taken to saturate the water with common salt to diminish the solubility of the gases. It is well to time the collection of issuing gas in a graduated tube. A comparison of the rate at which the gases come out with the rate at which they are passed in, frequently gives valuable information as to the exact course of the reaction.

356. If the products are partly or entirely *liquid,* the reaction tube is connected with a condenser. When the substances are only slightly volatile this may be simply a double-necked flask. When the volatility, at room temperature, is considerable, a U-tube is employed from the bottom of which a tube leads down into a flask in which the liquid collects. The U-tube is placed in an inverted tubulated bell-jar which is filled with cold water, ice, or a freezing mixture. The gas issuing from the other limb of the U-tube is collected over water and measured.

357. Solid reaction products are collected by prolonging the re-

action tube and cooling the further end. The tube should be long enough to project a considerable distance from the furnace and the end should be inclined downward so that condensed liquids will not run back towards the catalyst.

HYDROGENATIONS BY MEANS OF NICKEL

358. In Chapter II the conditions have been described under which *nickel* may be used to advantage as a catalyst for hydrogenations (53), and methods have been given for obtaining a metal of excellent catalytic properties. Nickel reduced at a red heat below 700° is capable of effecting all sorts of hydrogenations and in particular can hydrogenate benzene to cyclohexane;[10] but that reduced above 750°, or which has been heated to that temperature after having been reduced at a lower, is incapable of hydrogenating benzene, is no longer pyrophoric and does not gain in weight when exposed to cold air. It is then capable of only certain hydrogenations, such as the reduction of nitro derivatives.

359. As has been stated above (112), the presence of chlorine, bromine, or iodine, even in traces, in the metal paralyzes its catalytic activity. An oxide prepared by precipitation from the chloride can not be used, but good results can be obtained with an oxide produced by calcining the sulphate at a red heat.

Whatever care one may take, it is never possible to avoid all the causes of poisoning the metal catalyst and particularly in consequence of the progressive fouling of the metal which is more or less rapid according to the work done with it, a gradual diminution of the catalytic power, its *senilescence*, so to speak, is noticed.

360. Darzens believes that nickel exists in three forms, α, β, and γ. The very active γ form is said to be obtained by reduction below 260° and is considered unstable, remaining in metastable state below 260°. Above that temperature it passes into the less active β nickel, then at a bright red into the α form which is entirely inactive for hydrogenations.[11] According to this author the power to hydrogenate benzene belongs exclusively to γ nickel, which is contrary to the observations of Sabatier and Espil quoted above. These transformations of γ nickel, rapid at high temperatures, would take place slowly even at low temperatures and would explain the senilescence of the metal apart from many poisoning effects.[12]

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[10] Sabatier and Espil, *Bull. Soc. Chim.* (4), **15**, 779 (1914).
[11] Darzens, *Bull. Soc. Chim.* (4), **15**, 771 (1914).
[12] Darzens, *Compt. rend.*, **139**, 869 (1904).

361. Choice of Reaction Temperature. A given hydrogenation can be realized only within a well-defined temperature interval.

In practice, a lower temperature limit is set by the necessity of maintaining in the vapor state in the reaction tube, not only the compounds to be transformed but also the products of the reaction.

To a certain extent elevation of temperature accelerates the reaction and consequently raises the proportion of the substance hydrogenated during its passage through the tube. But beyond a certain limit, sometimes not far above the temperature at which the reaction begins, there is a profound modification of the phenomenon, it being possible to completely reverse the reaction in some cases. Thus the hydrogenation of benzene may be accomplished as low as 70°, and it increases in velocity as the temperature is raised till a maximum is reached at 180–200°. Then it decreases till 300° is reached, at which benzene is no longer hydrogenated, but, on the contrary, cyclohexane is decomposed into benzene and hydrogen.

362. By hydrogenating around 300°, the aromatic nucleus remains almost unaffected while any unsaturated side-chains are hydrogenated.[13] Thus *styrene*, $C_6H_5CH : CH_2$, hydrogenates almost completely at 300° to *ethyl-benzene*, $C_6H_5.CH_2.CH_3$, while if the temperature be reduced to 180°, this is further changed into *ethyl-cyclohexane*, $C_6H_{11}.CH_2.CH_3$.

If the temperature is raised above 300°, the aromatic nucleus is, little by little, broken up, and particularly in the case of benzene the reaction:

$$C_6H_6 + 9H_2 = 6CH_4$$
$$\underline{\text{methane}}$$
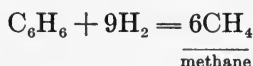
tends to become more and more important.[14]

363. When a compound can add several molecules of hydrogen in succession, we can sometimes contrive, by suitably choosing the temperatures, to produce one after the other of the various combinations.[15] In the hydrogenation of anthracene over nickel, at 180°, perhydro-anthracene, $C_{14}H_{24}$, is obtained along with the dodecahydro-, at 200°, the octohydro-, and at 260°, the tetahydro-anthracene.[16]

364. The easy hydrogenations are those which take place over a wide range of temperatures, as the saturation of ethylene bonds or the reduction of nitro compounds. The more difficult cases are those

[13] SABATIER and MURAT, *Ann. de Chim.* (9), **4**, 255 (1915).

[14] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 334 (1905).

[15] SABATIER and MAILHE, *Compt. rend.,* **137**, 240 (1903).

[16] GODCHOT, *Ann. Chim. Phys.* (8), **12**, 468 (1907).

where the possible temperature interval is narrow, as is the case in the hydrogenation of the aromatic nucleus, especially with diphenols, pyrogallol,[17] benzoic esters, and quinoline.[18]

365. As has been stated above (167), the hydrogenating activity of nickel is attributed to the rapid formation of a hydride formed directly by the hydrogen gas on the surface of the metal. This hydride is readily dissociated, and if it is brought into contact with substances capable of taking up hydrogen, it gives it to them very rapidly, regenerating the metal which can again form the hydride, repeating these reactions indefinitely.

The well-attested impossibility of carrying on all sorts of hydrogenations with any sort of nickel leads to the idea that there are several stages of combination with hydrogen. The nickel produced above 700° can doubtless form only the first hydride, comparable to that formed by copper, and capable of reacting with nitro groups or with an ethylene hydrocarbon. Only powerful nickel, such as is furnished by the reduction at a low temperature of the oxide prepared from the nitrate, can form a perhydride capable of hydrogenerating the aromatic nucleus (167).

RESULTS OBTAINED BY HYDROGENATION OVER NICKEL IN GASEOUS SYSTEM

366. The results obtained by hydrogenation over reduced nickel can be divided into four groups:

1. Simple reductions without fixation of hydrogen,
2. Reductions with simultaneous fixation of hydrogen,
3. Addition of hydrogen to molecules which contain multiple bonds between various atoms,
4. Hydrogenations accompanied by decomposition of the molecule.

REDUCTIONS EFFECTED WITHOUT FIXATION OF HYDROGEN

367. The reduction effected by the aid of nickel corresponds most frequently to the elimination of oxygen in the form of water; it can also remove sulphur as hydrogen sulphide.

368. **Nitrous Oxide.** The first case is furnished by nitrous oxide which is reduced to nitrogen, even at the ordinary temperature, with-

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[17] SABATIER, *Berichte,* **44,** 1997 (1911).
[18] SABATIER and MURAT, *Compt. rend.,* **158,** 309 (1914).

out any production of ammonia or hydrazine. By increasing the proportion of nitrous oxide in the hydrogen, the heat evolved raises the first portions of the nickel to incandescence, and there results a partial decomposition of the nitrous oxide with the appearance of red nitrogen peroxide, the hydrogenation of which carried on by the neighboring hot nickel gives a little ammonia.[19]

369. Aromatic Alcohols. The hydrogenation of aromatic alcohols over nickel at 350–400° replaces the hydroxyl group by hydrogen and leads to the corresponding aromatic hydrocarbon.[20]

Benzyl alcohol is changed to *toluene, phenylethyl alcohol* to *ethylbenzene, benzhydrol,* $C_6H_5.CH(OH).C_6H_5$, is changed quantitatively into *diphenyl-methane,* $C_6H_5.CH_2.C_6H_5$, and *phenyl-p.cresyl carbinol,* into *phenyl-p.cresyl-methane.*

Likewise, vapors of *triphenyl carbinol,* carried along by benzene vapors and hydrogen over nickel at 400°, readily yield *triphenyl-methane.*

This reaction is particularly easy when the alcoholic hydroxyl is attached to a carbon atom adjoining a carbon atom united to hydrogen in the same paraffine side-chain. The mechanism of the reaction may then correspond to a dehydration into the phenyl-ethylene hydrocarbon, which is at once hydrogenated into the saturated hydrocarbon. Thus *tolyl-dimethyl carbinol,* $CH_3.C_6H_4.C(OH).(CH_3)_2$, which is very readily dehydrated, gives with a nickel only slightly active *cymene,* which may be transformed into menthane if an active nickel is used below 180°.[21]

370. Phenols and Polyphenols above 250°. *Phenol* hydrogenated at 250 to 300° over nickel, gives only *benzene* with the elimination of water:

$$C_6H_5.OH + H_2 = H_2O + C_6H_6.$$
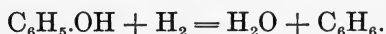
But the reaction is slow and much of the phenol passes by unchanged. If the attempt is made to hasten the reaction by raising the temperature, the benzene is attacked with the formation of methane. The three *cresoles* behave the same way and yield toluene.

At 250° the *diphenols* (pyrocatechin, resorcine, and hydroquinone) undergo a similar reaction, the hydroxyl groups being successively replaced by hydrogen, phenol being first formed and then benzene.[22]

[19] SABATIER and SENDERENS, *Compt. rend.,* **135,** 278 (1902).

[20] SABATIER and MURAT, *Ann. de Chim.* (9), **4,** 258 (1915).

[21] SMIRNOF, *J. Russian Phys. Chem. Soc.,* **41,** 1374 (1909).

[22] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 429 (1905).

371. Furfuryl Alcohol. This alcohol submitted to a careful hydrogenation over nickel at 190°, yields *methylfurfurane*.[23]

$$\begin{array}{ccc}
\text{CH}-\text{CH} & & \text{CH}-\text{CH} \\
\text{CH} \quad \text{C.CH}_2\text{OH} & \rightarrow & \text{CH} \quad \text{C.CH}_3 \\
\diagdown \;\diagup & & \diagdown \;\diagup \\
\text{O} & & \text{O}
\end{array}$$
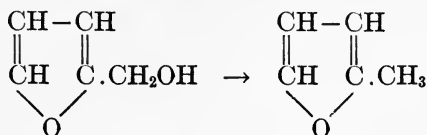
372. Carbon Disulphide. Carbon disulphide submitted to hydrogenation over nickel below 200°, gives an addition product having a very disagreeable odor (492), but if the operation is carried on at 450–500°, in excess of hydrogen, the reaction takes place thus:

$$CS_2 + 2H_2 = 2H_2S + C.$$
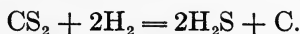
This reaction is utilized in freeing *coal gas* from carbon disulphide which it contains up to 0.02%.

The gas is freed from hydrogen sulphide by chemical purification in the Laming absorbers and is then heated to 400° and passed through steel tubes 7 cm. in diameter containing porous earth impregnated with nickel and heated to between 400 and 500°. The gas is cooled when it passes out of the tubes and is freed by a second passage through the chemical absorbers from the hydrogen sulphide which has been formed. On account of the deposition of carbon and also on account of a certain sulphurization of the surface, the nickel loses its activity rather rapidly. It is regenerated by passing air which burns up the carbon and converts the nickel to the oxide which is again reduced by the first portions of gas that enter. The installation of this process at the Greenwich gas works is capable of handling 500,000 cu. m. per day.[24]

REDUCTIONS WITH SIMULTANEOUS FIXATION OF HYDROGEN

373. These reductions can be considered as true *substitutions* of hydrogen either for oxygen or, in a few cases, for the halogens, chlorine or bromine.

374. Oxides of Nitrogen. Although the oxides of nitrogen are outside of the scope of this treatise, yet their close connection with organic nitro and nitroso compounds justifies us in mentioning the conditions of their catalytic hydrogenation.

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[23] PADOA and PONTI, *Lincei*, **15** (2), 610 (1909); *C.*, **1907** (1), 570.

[24] CARPENTER, *J. Gas Lighting*, **126**, 928 (1914). EVANS, *J. Soc. Chem. Ind.*, **34**, 9 (1915).

Nitric oxide, NO, is readily reduced above 180° with the formation of ammonia and water according to the equation:

$$NO + 5H = NH_3 + H_2O.$$
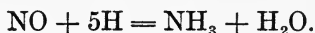
But the nitric oxide reacts with the ammonia more and more rapidly the higher the temperature, giving nitrogen and water according to the equation:

$$2NH_3 + 3NO = 5N + 3H_2O.$$
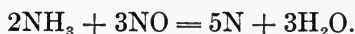
By progressively increasing the proportion of nitric oxide, the metal becomes incandescent and this greatly increases the production of nitrogen.[25]

375. If hydrogen which has passed through a thin layer of liquid *nitrogen peroxide*, cooled a little below 0°, is passed over cold reduced nickel, a slight evolution of heat is noticed which is due to the formation of *nickel nitride*.[26]

If it is heated to 180°, white fumes of *ammonium nitrate* and *nitrite* appear which, when hydrogenated further, give ammonia and water. We have finally:

$$NO_2 + 7H = NH_3 + 2H_2O.$$
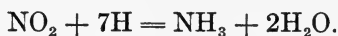
If the proportion of nitrogen peroxide in the hydrogen is increased by warming the vessel containing the nitrogen peroxide, the white fumes are produced in abundance and incandescence of the nearest portion of the metal layer is noticed and a violent explosion soon takes place.[25]

376. The vapors of *nitric acid* mixed with hydrogen and passed over nickel at 290° give much ammonium nitrate. At 350° only water, ammonia, and free nitrogen are produced.[25]

377. **Aliphatic Nitro Compounds.** *Nitromethane* is completely hydrogenated between 150 and 180° to *methyl-amine* without any side reactions. But above 200° and particularly towards 300°, there is partial hydrogenation of the methyl-amine into methane and ammonia:[27]

$$CH_3 \cdot NO_2 + 4H_2 = CH_4 + NH_3 + 2H_2O$$
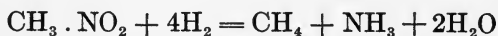
and at the same time, the formation of certain amounts of dimethyl- and trimethyl-amines along with the ammonia by a reaction identical with that which has been described in the hydrogenation of nitriles.

[25] SABATIER and SENDERENS, *Compt. rend.*, **135**, 278 (1902).
[26] SABATIER and SENDERENS, *Ann. Chim. Phys.* (7), **7**, 413 (1895).
[27] SABATIER and SENDERENS, *Compt. rend.*, **135**, 226 (1902).

Likewise *nitroethane* is readily transformed at 200° into *ethyl-amine* accompanied by *diethyl-amine*, *triethyl-amine* and ammonia. At 350° the matter is complicated by the formation of *ethane* and also of *methane* which is due to the dissociation of the ethane by the nickel. But this secondary formation of the hydrocarbon is less than with nitromethane.

378. Aromatic Nitro Compounds. Above 200° *nitrobenzene* is rapidly transformed into *aniline*, but the aniline is immediately hydrogenated to form cyclohexylamine, etc. (466). If only slightly active nickel is used, the nucleus is not hydrogenated and aniline is the only product.[28]

Above 250°, a part of the nitrobenzene is reduced to benzene and ammonia:

$$C_6H_5 . NO_2 + 4H_2 = C_6H_6 + NH_3 + 2H_2O.$$
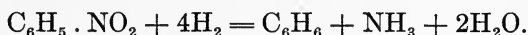
This reaction is more in evidence above 300° and even the benzene is broken up to form methane:

$$C_6H_5 . NO_2 + 13H_2 = 6CH_4 + NH_3 + 2H_2O.$$
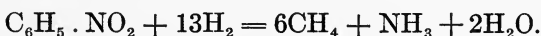
Ortho and *meta nitrotoluenes* behave similarly with a nickel catalyst at 200 to 250°, and as the further hydrogenation of the resulting toluidines does not take place readily, the toluidines are obtained nearly pure.

These reactions can be used in the factory and it has been proposed to prepare aniline by passing a current of hydrogen and steam through nitrobenzene maintained at 120° and then into a long tube containing reduced nickel also kept at 120°. A theoretical yield is claimed.[29]

379. *α-Nitronaphthalene* gives at 300° beautiful white needles of *α-naphthyl amine*, but if the temperature is raised to 330°, or better, to 380°, ammonia is evolved and there condense, along with the diminishing naphthyl amine, *naphthalene* and *tetrahydronaphthalene*.[28] We have:

$$C_{10}H_7 . NO_2 + 4H_2 = C_{10}H_8 + NH_3 + 2H_2O.$$
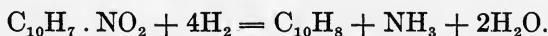
380. *Dinitro* derivatives are transformed with the same facility. The dinitrobenzenes give the corresponding diamines at 190–210°. At 250°, there is the splitting off of ammonia to form aniline.[30] Like-

[28] Sabatier and Senderens, *Compt. rend.*, **135**, 226 (1902).

[29] Farbw. Meister, Lucius and Brüning, *German patent*, 282,492 (1913).

[30] Mignonac, *Bull. Soc. Chim.* (4), **7**, 154 (1910).

wise the *dinitrotoluenes* yield the *cresyl-diamines* at 175–180°, but above 190° ammonia is split off and the toluidines are the chief products.[31]

381. The nitrophenols hydrogenated over nickel at 160–190°, yield the amino-phenols regularly; but there are simultaneously produced certain amounts of ammonia and phenol and also a little aniline.[32]

382. **Esters of Nitrous Acid.** It is stated in all the textbooks that a fundamental distinction between the nitrohydrocarbons and their isomers, the nitrites, is that the nitro compounds yield amines on hydrogenation, while the nitrous esters are either not affected or give the alcohols and ammonia without any amine.

Gaudion has found that nitrous esters are regularly hydrogenated by nickel to give amines exactly like their isomers. This author has worked at 180° with *methyl* and *ethyl nitrites,* at 200° with *propyl* and *isopropyl,* and at 220° with *isobutyl* and *isoamyl.*

As a consequence of the secondary reaction already mentioned, all three amines, primary, secondary, and tertiary, are obtained, the secondary always in the largest quantity. Thus from isoamyl nitrite, 31% mono-, 62% di-, and 7% tri-isoamyl-amines are obtained.

The discussion of these facts has led Gaudion to assume that there is an isomerization of the nitrous esters into the nitro bodies at the temperature of the reaction.[33]

The reality of this transformation by heat alone has since been established. It begins at 100° and is rapid at 125–130°.[34]

By carrying on the hydrogenation at low temperatures, around 125–130°, over nickeled asbestos, the unchanged nitrous esters are hydrogenated along with the nitro bodies into which they are partly isomerized so that there is simultaneous production of ammonia and the corresponding alcohol from the nitrite and of the amine from the nitro compound; while when a nitro compound is hydrogenated, the *primary amine* alone is formed without any secondary or tertiary. This is the case with *methyl, ethyl, propyl, isobutyl* and *isoamyl nitrites.*[35]

383. **Oximes.** In the aliphatic series, *aldoximes* and *ketoximes* are readily reduced by hydrogen in the presence of nickel at 180–220° to give primary and secondary amines with a small amount of tertiary.

With *acetoxime,* the chief product is diethyl amine, while with

[31] MIGNONAC, *Bull. Soc. Chim.* (4), **7**, 823 (1910).
[32] MIGNONAC, *Bull. Soc. Chim.* (4), **7**, 270 (1910).
[33] GAUDION, *Ann. Chim. Phys.* (8), **25**, 129 (1912).
[34] NEOGI and CHOWDURG, *J. Chem. Soc.,* **109**, 701 (1916).
[35] NEOGI and CHOWDURG, *J. Chem. Soc.,* **111**, 899 (1917).

heptaldoxime, $C_6H_{13} . CH : N . OH$, the primary amine is the most abundant.

The *oxime* of *acetone* gives *isopropyl-amine,* with twice as much of the *di-* and a little of the *tri-isopropyl-amine.* Analogous results are obtained with *butanoxime*(2), $C_2H_5(CH_3)C : N . OH$, *pentanoxime*(2), *pentanoxime*(3), and *2,4-dimethyl pentanoxime*(3).[36]

By this means the *secondary amines* from *secondary alcohols* can be prepared with good yields, a class of substances otherwise difficult to obtain.

384. This method can also be applied to aromatic aldoximes in spite of the difficulty of vaporizing them without decomposition. It is best to operate with a rapid current of hydrogen and at as low a temperature as possible. *Acetophenone-oxime,* $C_6H_5 . C(: NOH)$.- CH_3, carried thus over nickel at 250–270°, gives a small amount of the primary amine, $C_6H_5 . CH(NH_2) . CH_3$, a larger amount of the secondary amine and some acetophenone regenerated by the action of the resulting water on the oxime.

The results are not so good with *propiophenone-oxime,* from which small amounts of the primary and secondary amines are obtained along with much *phenylpropylene* and *phenylpropane,* and still poorer results are obtained with *butyrophenone oxime.*

On the contrary, the method serves well with *benzophenone-oxime* from which up to 70% of the primary amine, $(C_6H_5)_2CH . NH_2$, is obtained with a certain amount of the secondary.[37]

385. The *ketoximes* of the *cycloparaffines* react in an analogous manner.

The hydrogenation of *cyclohexanone-oxime* over nickel at 190–200° gives cyclohexyl-amine regularly with a little dicyclohexyl amine and aniline.[38] The results are not so good with the three *methyl-cyclohexanone-oximes,* as the yields of the amines are poor.

The hydrogenation of *cyclopentanone-oxime,* $\begin{matrix} CH_2 . CH_2 \\ \cdot \qquad\qquad\; \\ CH_2 . CH_2 \end{matrix}\!\!\Big\rangle C : NOH,$

over nickel at 180°, proceeds smoothly to give a mixture of the three cyclopentyl-amines, the secondary forming half of the product and the primary and tertiary, each about one-fourth. Analogous results are obtained with *methyl-cyclopentanone-oxime.*[39]

[36] MAILHE, *Compt. rend.,* **140**, 1691 (1905), *Ibid.,* **141**, 115 (1905) and *Bull. Soc. Chim.* (4), **15**, 327 (1914).

[37] MAILHE and MURAT, *Bull. Soc. Chim.* (4), **9**, 464 (1911).

[38] AMOROUX, *Bull. Soc. Chim.* (4), **9**, 214 (1911).

[39] SABATIER and MAILHE, *Compt. rend.,* **158**, 985 (1914).

Menthone-oxime yields the primary and secondary amines and a little regenerated menthone.[40]

Camphoroxime, when hydrogenated over nickel gives the corresponding amine in good yield.[41]

386. Aliphatic Amides. *Acetamide* is readily hydrogenated at 230° by nickel with the production of water and *ethylamine* and also some *dimethylamine,* due to the decomposition of the primary amine by the metal, and a small amount of ammonia.

Propionamide, $CH_3 . CH_2 . CO . NH_2$, gives results entirely similar.[42]

387. Ethyl Acetoacetate. Ethyl acetoacetate, the ester of an unstable β-keto-acid, gives, when hydrogenated over nickel, a triple reaction: [43]

1. A hydrogenation by substitution:

$$CH_3 . CO . CH_2 . CO_2 . C_2H_5 \rightarrow \underline{CH_3 . CH_2 . CH_2 . CO_2 . C_2H_5.}$$
$$\text{ethyl butyrate}$$
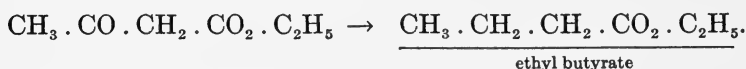
2. A breaking up of the molecule into the fragments $CH_3 . CO .- CH_2-$ and $-CO_2 . C_2H_5$ which are hydrogenated separately, the first into *acetone* and then *isopropyl alcohol* (435), the second into ethyl formate which is decomposed, under the reaction conditions, into ethyl alcohol and carbon monoxide which may go into methane (867).

3. A condensation of the molecule with the formation of solid *dehydroacetic acid,* $(CH_2 . CO)_4$, which is produced by the action of heat alone on ethyl acetoacetate,[44] and which the presence of the nickel, without the hydrogen, causes to be formed at 250°:

$$2 CH_3 . CO . CH_2 . CO_2 . C_2H_5 = (CH_2CO)_4 + 2C_2H_5 . OH.$$
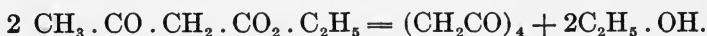
388. Aromatic Aldehydes. Contrary to what takes place with aliphatic aldehydes, the hydrogenation of aromatic aldehydes over nickel does not reduce them to alcohols, but tends to replace the oxygen by hydrogen, H_2, to give the aromatic hydrocarbons, which below 250° may be more or less hydrogenated to the cyclohexane hydrocarbons. There is, at the same time, some decomposition of the aldehyde into the hydrocarbon and carbon monoxide (618). Thus between 210 and 235°, *benzaldehyde* gives toluene and benzene according to the two reactions:

$$C_6H_5 . CHO + 2H_2 = H_2O + C_6H_5 . CH_3$$
$$C_6H_5 . CHO = CO + C_6H_6,$$
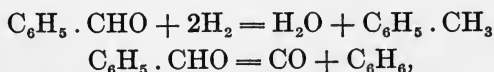
[40] MAILHE and MURAT, *Bull. Soc. Chim.* (4), **9**, 464 (1911).
[41] ALOY and BRUSTIER, *Bull. Soc. Chim.* (4), **9**, 734 (1911).
[42] MAILHE, *Bull. Soc. Chim.* (3), **35**, 614 (1906).
[43] SABATIER and MAILHE, *Bull. Soc. Chim.* (4), **3**, 232 (1908).
[44] GEUTHER, *Zeit. f. Chem.,* **2**, 8 (1866).

and these are accompanied by certain proportions of *methylcyclo-hexane* and *cyclohexane,* the carbon monoxide being partly reduced to *methane* (393).[45]

389. Aromatic Ketones. The hydrogenation of aryl-aliphatic ketones, effected rapidly over a nickel of only moderate activity or at a temperature above 250°, is limited to replacing the ketone oxygen by H_2 with the production of the corresponding aromatic hydrocarbon. Thus *acetophenone,* $C_6H_5 . CO . CH_3$, gives *ethyl-benzene,* $C_6H_5 . C_2H_5$; *methyl-p.cresyl ketone,* $CH_3 . C_6H_4 . CO .-CH_3$, yields *p.methyl-ethyl benzene; p.tert-butyl-acetophenone,* $(CH_3)_3C . C_6H_4 . CO . CH_3$, gives *p.ethyl-tert-butyl-benzene;* and *benzyl-acetone,* $C_6H_5 . CH_2 . CH_2 . CO . CH_3$, yields *butyl-benzene.*[46]

But when the hydrogenation is carried on at 180°, with an active nickel which is capable of hydrogenating the nucleus, the aromatic hydrocarbon is reduced to the cyclohexane derivative. One can be sure of avoiding this complication if nickel is used that has been so altered that it can not hydrogenate benzene or if the operation is carried on about 300°, the temperature at which cyclohexane deriva-tives are dehydrogenated even in excess of hydrogen.[47]

It is the same way with *diaryl ketones* which are quantitatively reduced to the corresponding hydrocarbons by nickel at 300°.

Thus *benzophenone* at 300° is entirely reduced to *diphenylmethane,* while with an active nickel at 160°, *dicyclohexylmethane* is formed.

Desoxybenzoïne, $C_6H_5 . CH_2 . CO . C_6H_5$, yields *dibenzyl,* $C_6H_5 .-CH_2 . CH_2 . C_6H_5$, at 350°. Likewise *dibenzyl ketone,* $C_6H_5 . CH_2 .-CO . CH_2 . C_6H_5$, is 70% transformed at 400° into symmetrical *diphenylpropane,* which is accompanied by *toluene* formed by the breaking up of the molecule with the separation of carbon monoxide which is reduced to methane. The same hydrocarbon is formed by the hydrogenation over nickel at 350° of *phenyl-phenylethyl ketone,* $C_6H_5 . CO . CH_2 . CH_2 . C_6H_5$.[48]

390. Likewise *methyl-α-naphthyl-ketone* yields *α-ethylnaphtha-lene,* and *methyl-β-naphthyl* and the *propyl-naphthyl ketones* behave in a similar manner.[49]

Hexahydroanthrone is hydrogenated at 200° into *octohydroanthra-cene:*[50]

[45] Sabatier and Senderens, *Compt. rend.,* **137,** 301 (1903).
[46] Darzens, *Compt. rend.,* **139,** 868 (1904).
[47] Sabatier and Murat, *Ann. Chim.* (9), **4,** 263 (1915).
[48] Sabatier and Murat, *Ann. Chim.* (9), **4,** 264 (1915).
[49] Darzens and Rost, *Compt. rend.,* **146,** 933 (1908).
[50] Godchot, *Bull. Soc. Chim.* (4), **1,** 712 (1907).

$$C_6H_{10} \underset{CO}{\overset{CH_2}{<\quad>}} C_6H_4 \;\rightarrow\; C_6H_{10} \underset{CH_2}{\overset{CH_2}{<\quad>}} C_6H_4$$
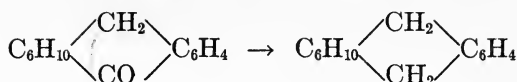
Likewise *methyl*(1)*cyclopentanone*(3) is advantageously transformed at 250° into *methylcyclopentane*.[51]

$$Dihydrocamphorone, \; CH_3.CH \underset{CH_2.CH_2}{\overset{CO}{<\quad>}} CH.CH(CH_3)_2, \text{ is hy-}$$
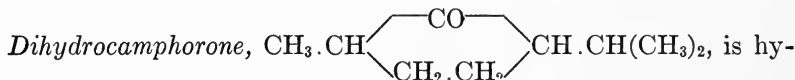
drogenated at 180° to form *methyl-isopropyl-cyclopentane*, boiling at 132°.[52]

391. Aromatic Diketones. Similarly to the monoketones, the aromatic diketones, when hydrogenated over nickel, give the hydrocarbons.[53]

Dibenzoyl, $C_6H_5 . CO . CO . C_6H_5$, which is an α diketone, is hydrogenated over nickel at 220° to symmetrical *diphenylethane*, or *dibenzyl*, $C_6H_5 . CH_2 . CH_2 . C_6H_5$, beautiful crystal flakes, without appreciable secondary reactions.

Benzoïne, $C_6H_5 . CH(OH) . CO . C_6H_5$, gives the same hydrocarbon as the sole product at 210–220°.

Benzoyl-acetone, $C_6H_5 . CO . CH_2 . CO . CH_3$, which is a β diketone, when hydrogenated over nickel at 200°, reacts in two ways:

1. *Butylbenzene* is formed to an extent of about 80%.

2. Following a general tendency of β diketones, there is a breaking up into two fragments, $C_6H_5 . CO-$ and $-CH_2 . CO . CH_3$, which are hydrogenated separately, the one into toluene and the other into acetone, and then into isopropyl alcohol.

392. Anhydrides of Dibasic Acids. The anhydrides of dibasic acids which have been submitted to hydrogenation at low temperatures, have given only the corresponding lactones.

Succinic anhydride gave *butyrolactone:* [54]

$$\underset{CH_2.CO}{\overset{CH_2.CO}{\cdot \quad >}} O \;\rightarrow\; \underset{CH_2.CO}{\overset{CH_2.CH_2}{\cdot \quad >}} O.$$
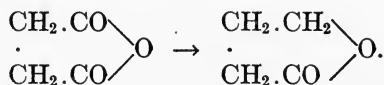
Over nickel at 200°, *phthalic anhydride* yields *phthalid* quantitatively:

$$C_6H_4 \underset{CO}{\overset{CO}{<\quad>}} O \;\rightarrow\; C_6H_4 \underset{CO}{\overset{CH_2}{<\quad>}} O.$$
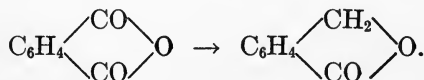
[51] Zelinsky, *Berichte*, **44**, 2781 (1911).
[52] Godchot and Taboury, *Compt. rend.*, **156**, 470 (1913).
[53] Sabatier and Mailhe, *Compt. rend.*, **145**, 1126 (1907).
[54] Eijkmann, *Chem. Weekblad*, **4**, 191 (1907).

Even by operating at 130° with very active nickel it is impossible to replace the second carbonyl.[55]

In the same manner *camphoric anhydride* is changed into *campholid* exclusively: [54]

$$C_8H_{14} \underset{CO}{\overset{CO}{<}} O \rightarrow C_8H_{14} \underset{CO}{\overset{CH_2}{<}} O.$$
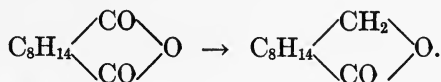
393. Carbon Monoxide. The direct hydrogenation of carbon monoxide over nickel gives a simple method for the synthesis of *methane:*

$$CO + 3H_2 = H_2O + CH_4.$$
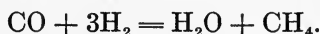
The reaction commences around 180–200° and goes on rapidly without complications at 230–250°. With the theoretical mixture of hydrogen and carbon monoxide, 3:1, the reaction is practically complete, the resulting gas being nearly pure methane.

The nickel is not sensibly altered by the reaction when it is carried on below 250° and can be used indefinitely. On cooling it is found to be slightly carbonized but still pyrophoric and completely soluble in dilute hydrochloric acid without carbonaceous residue.

The reaction is less complete when the carbon monoxide is in excess; in an experiment carried out with 85 volumes of carbon monoxide to 51 volumes of hydrogen, almost one third of the hydrogen passed through the tube without combining, although the velocity of the gas was no greater than in the experiment quoted above.

394. If the operation is carried on above 250°, complications arise due to the special effect that finely divided nickel has on carbon monoxide which it breaks up into *carbon* and *carbon dioxide* (614):

$$2CO = C + CO_2.$$

The carbon dioxide which is thus formed is partially hydrogenated. Its proportion is greater, the higher the temperature, since the secondary reaction which produces it is greatly accelerated by rise of temperature.

Thus when operating at 380° with the theoretical mixture which gives methane completely at 250°, a gas is obtained which contains:

Carbon dioxide .... 10.5% by vol.
Methane 67.9
Hydrogen 21.6

[54] EIJKMANN, *Chem. Weekblad,* **4,** 191 (1907).
[55] GODCHOT, *Bull. Soc. Chim.* (4), **I,** 243 (1907).

At the same temperature, *water gas,* equal volumes of hydrogen and carbon monoxide, gives 52.6% carbon dioxide, 39.8% methane, and 7% hydrogen.

When the percentage of carbon monoxide is still further increased, the hydrogenation is greatly weakened; much hydrogen passes through and the proportion of carbon dioxide becomes very large.[56]

395. Carbon Dioxide. Like the monoxide, carbon dioxide is readily hydrogenated over nickel to form *methane:*

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$
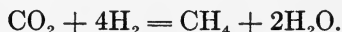
The reaction begins at a higher temperature than that with carbon monoxide, namely, around 230°, and is rapid above 300° and does not offer any considerable complications up to 400°. The theory calls for four volumes of hydrogen to one of carbon dioxide. With gas mixtures containing a larger proportion of hydrogen, the carbon dioxide disappears almost completely.

Thus in an experiment with 82% of hydrogen and 18% carbon dioxide, passed through the tube containing the nickel at the rate of 55 cc. per minute, the issuing gas contained:

With the nickel at 258° .... 17.2% by vol. carbon dioxide
    "   "   "   " 283° .... 0.5% "   "   "   "

396. Carried on at 300° with an excess of hydrogen, this reaction gives a very advantageous method for preparing *pure methane* if liquid air is available for condensing the methane. The gas is washed with caustic potash to free it from traces of carbon dioxide, dried and the methane condensed, leaving the hydrogen as gas.[57]

397. Application to the Manufacture of Illuminating Gas. The production of methane by the direct hydrogenation of carbon dioxide over nickel can be used for the commercial preparation of a gas rich in methane having a high calorific power and capable of being used either for heating or for lighting by using incandescent mantles.[58]

If hydrogen is available (produced electrolytically or by the action of iron on steam at a red heat), the hydrogenation of carbon dioxide over nickel at 300 to 400° is an excellent way to prepare methane.[59]

But the preparation of the hydrogen costs too much for it to be used for the manufacture of illuminating gas. One must start with

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[56] SABATIER and SENDERENS, *Compt. rend.,* **134,** 514 (1902).

[57] SABATIER and SENDERENS, *Compt. rend.,* **134,** 689 (1902).

[58] SABATIER, *VI Internat. Cong. Pure and App. Chem.,* Rome, 1906, IV sect. p. 188.

[59] SABATIER, *French patent,* 356,471, June 17, 1905.

a cheap commercial gas such as *water gas, Riché gas, Siemens gas,* etc. Various methods may be followed.

398. *First method.* Water gas obtained by the action of steam on red-hot carbon varies in composition according to the temperature at which it is prepared.

At a bright red, there are equal volumes of hydrogen and carbon monoxide:

$$C + H_2O = CO + H_2.$$

At a lower temperature (a very dull red) there are only carbon dioxide and hydrogen:

$$C + 2H_2O = CO_2 + 2H_2.$$
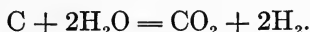
If the temperature is intermediate (cherry red), the reaction is intermediate:

$$2C + 2H_2O = CO + CO_2 + 3H_2.$$

If in this case the carbon dioxide be removed by any method there remains the mixture $CO + 3H_2$. The carbon dioxide may be absorbed by a solution of potassium carbonate which is changed to the bicarbonate, but is regenerated with evolution of carbon dioxide by boiling. The carbon dioxide may be solidified by refrigeration or absorbed in cold water under pressure. The residual mixture, $CO + 3H_2$, is converted into pure methane by passing over nickel at 230–250°, 5 volumes of water gas thus furnishing 1 volume of methane. A practical difficulty arises from the fact that the catalyst must be kept between 230 and 250°, since above 250° there is charring with loss of carbon and fouling of the nickel resulting in a rapid diminution of its catalytic power.

399. *Second Method.* The operation is carried on in two phases: *Water gas* prepared at a high temperature and very nearly $CO + H_2$ is passed over nickel at 400 to 500°, by which all the carbon *monoxide disappears* forming either methane with the available hydrogen, or splitting up into carbon dioxide (614) and finely divided carbon which is deposited on the nickel. If from the gas so produced, the carbon dioxide is absorbed, the remainder is very rich in methane. For the conditions cited above (394), the composition would be 83.8% methane and 15% hydrogen with a calorific power of 7,800 calories per cu. m., while the original gas had only 2,880. This is the *gas of the first phase.*

If steam be passed over the intimate mixture of carbon and nickel obtained above, kept at 400 to 500°, the carbon reacts rapidly tending to give hydrogen and carbon dioxide which being in the nascent

state react to give a certain proportion of methane. The final product is a mixture of hydrogen, methane and carbon dioxide and if the carbon dioxide is eliminated, there remains a mixture of hydrogen and methane of high calorific power which can be used. This is the *gas of the second phase,* less rich in methane than the first. Its formation has eliminated the carbon from the nickel which is then ready to repeat the first phase of the reaction.[60]

400. *Third Method.* The *gas of the second phase* can be obtained alone by preparing at first the intimate mixture of nickel and carbon by the action of finely divided nickel on various gases rich in carbon monoxide such as Siemens gas or producer gas. The carbon monoxide disappears leaving carbon dioxide and carbon. It is sufficient to maintain this carbonaceous mass at 400 to 500° and pass superheated steam over it to have a mixture of methane, hydrogen and carbon dioxide which can be used after the latter is eliminated.[61]

401. *Fourth Method.* The two phases of the reaction that have just been described can be combined in practice. All that is required is to maintain finely divided nickel at 400 to 500° and pass over it a mixture of suitable proportions of *water gas* (or *Riché gas* [62]) and superheated steam. Under these conditions the carbon monoxide disappears and is replaced by hydrogen, methane and carbon dioxide, and if the latter is eliminated, we have in one operation a usable mixture of hydrogen and methane.

This method of operating appears economical. The amount of nickel required for the reaction is less than 1 k. for making 1 cu. m. of gas per hour. Besides, if the carbonated gases introduced are suitably purified and if this purification is completed by passing over copper turnings heated to 600°, the nickel may be said to retain its catalytic power indefinitely. By starting with water gas a gas is obtained having an average composition of 48% methane and 52% hydrogen and having a calorific power of 5,800 calories per cu. m. This gas does not contain an appreciable amount of carbon monoxide which is present in coal gas in considerable amount (from 8 to 15%) and which renders it decidedly toxic.

In fact the reactions that take place with these conditions under the influence of nickel between water gas and steam can be summed up in this equation:

$$5\,(\underline{CO + H_2}) + H_2O = 2CH_4 + 2H_2 + 3CO_2.$$
$$\text{water gas}$$
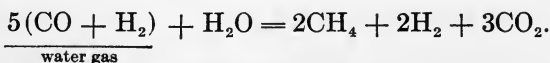
[60] Sabatier, *French patent,* 355,900, July 5, 1905.

[61] Sabatier, *French patent,* 355,900, 1905.

[62] The Riché gas is a mixture of carbon monoxide, hydrogen, methane and carbon dioxide prepared by heating woody or cellulose materials.

Theoretically 5 volumes of perfect water gas should give 2 volumes of the mixture containing 50% methane. In practice, as the water gas contains some carbon dioxide, about 3 volumes are required on the average for 1 volume of the finished gas.

402. The use of industrial refrigeration permits a very advantageous modification of the first process (398). The water gas should be prepared at the highest possible temperature so as to contain $CO + H_2$ and a little carbon dioxide and nitrogen. By suitable refrigeration 75% of the carbon monoxide can be liquefied and a mixture of $CO + 4H_2$ obtained which passing over nickel at 200 to 250° would furnish exactly the gas $CH_4 + H_2$ equivalent to coal gas. The refrigeration condenses all of the substances that may be toxic to the nickel (sulphurous gases, etc.) and hence guarantees the long life of the catalyst.

The carbon monoxide separated by the liquefaction may be used for heating the catalyzers or for driving motors.[63]

403. **Aromatic Halogen Derivatives.** The direct reduction of aromatic halogen derivatives by hydrogen in the presence of nickel may take place more or less readily: it is easy with chlorine derivatives, less easy for bromine derivatives, and difficult for iodine compounds; the reason being easy to find in the decreasing affinity of the halogens for hydrogen as we pass from chlorine to iodine, since the simultaneous formation of the hydro-acid determines the substitution of hydrogen.

When the vapors of *chlorbenzene* are carried by hydrogen over reduced nickel at 160°, a strong absorption of hydrogen is noted at once and a little *cyclohexane* is condensed without any *chlorcyclohexane*. The chlorine remains, fixed by the nickel, the surface of which loses all activity by being changed to the chloride. After a short time the chlorbenzene passes through unchanged.

But if the temperature is raised above 270° a vigorous evolution of hydrochloric acid is observed and a readily separated mixture of benzene and chlorbenzene is condensed. At the same time there is the formation of crystals of *diphenyl*.

In contact with nickel at 270° or above, chlorbenzene gives nickel chloride, and the liberated residue, C_6H_5-, combines with hydrogen to give benzene and unites with itself to form a small amount of diphenyl. But at this temperature the nickel chloride is reduced by hydrogen forming hydrochloric acid and regenerating the nickel which repeats the reaction indefinitely.

404. An analogous reduction is observed when the polychlor-

[63] Sabatier, *Second Congress on Refrigeration*, **i**, 115 (1912).

derivatives of benzene are acted on by hydrogen in the presence of nickel above 270°; the chlorine atoms are progressively replaced by hydrogen.

Thus *m.dichlorbenzene* gives a mixture containing:

Benzene 30%
Monochlorbenzene 60%
Unchanged dichlorbenzene 10%

p.Dichlorbenzene gives 35% benzene and 65% monochlorbenzene.

Perchlorbenzene, C_6Cl_6, acts in the same way at 270° and gives a mixture of the *trichlorbenzenes* (particularly the 1,2,4), *dichlorbenzenes*, monochlorbenzene, and benzene.

The presence of aliphatic side-chains and hydroxyl groups facilitates the reduction, the *chlortoluenes* being more readily reduced than chlorbenzene.

2,4,6-*Trichlorphenol* is readily reduced at 270° and gives 70% of *phenol* accompanied by monochlorphenols, particularly the *ortho*.

The reduction goes even better with amino derivatives, such as the *chloranilines* which give aniline hydrochloride at 270°.

The *chlornitrobenzenes* suffer simultaneous reduction of the nitro group and elimination of the chlorine, furnishing aniline hydrochloride at 270°.[64]

405. It can be foreseen that the reduction of *bromine* derivatives will be more difficult, since the temporary nickel bromide is less easily reduced by hydrogen. However, the reaction can be carried out well with *monobrombenzene* at 270° and also with *p.bromtoluene*, the *bromanilines* and the *bromnitrobenzenes*.

2,4,6-*Tribromphenol* readily yields phenol accompanied by *p.bromphenol* and 2,4-*dibromphenol*.

406. The difficulties are greater for the iodine derivatives. Iodobenzene passed over nickel with hydrogen at 270° gives no lasting evolution of hydriodic acid; some benzene and diphenyl are formed, but the reaction stops, since the nickel is not restored by the hydrogen and does not continue the reaction.

If pure hydrogen is passed into the tube, fumes of hydriodic acid appear, hence nickel iodide is reduced by hydrogen at 270° but not in the presence of iodobenzene, doubtless because this compound gives iodine to the nickel faster than the hydrogen can remove it. Practically, the reduction of iodobenzene can be forced by alternately passing pure hydrogen and hydrogen mixed with iodobenzene vapors

[64] Sabatier and Mailhe, *Compt. rend.*, **138**, 245 (1904).

over the nickel at 270°.   But under these conditions the metal is not a true catalyst.[65]

407. Esters of Halogenated Aliphatic Acids.   Vapors of ethyl *mono-*, *di-*, and *tri-chloracetates*, when passed over nickel at 300°, with excess of hydrogen, are reduced to *ethyl acetate*, the chlorine atoms being successively replaced by hydrogen.   *Ethyl bromacetate* is as readily reduced to *ethyl acetate*.[66]

[65] SABATIER and MAILHE, *Compt. rend.*, **138**, 245 (1904).

[66] SABATIER and MAILHE, *Compt. rend.*, **169**, 758 (1919).

CHAPTER IX

HYDROGENATIONS (Continued)

HYDROGENATIONS IN THE GAS PHASE — USE OF NICKEL (Continued)

ADDITION OF HYDROGEN

408. MANY hydrogenations correspond to the fixation of hydrogen by addition. This addition takes place either to free carbon, which is rare, or to complex molecules containing double or triple bonds between the atoms. We will examine these in the following order:

1. Direct fixation by carbon,
2. On double bond between two carbon atoms, so-called ethylene bond, C : C,
3. On triple bond between two carbon atoms, called the acetylene bond, C ⫶ C,
4. Triple bond between carbon and nitrogen, C ⫶ N,
5. Quadruple bond between carbon and nitrogen, C ⫶ N,
6. Double bond between carbon and an oxygen atom, C : O,
7. Aromatic nucleus,
8. Various rings,
9. Carbon disulphide.

1. Direct Fixation of Hydrogen by Carbon

409. Berthelot noted the direct union of hydrogen and carbon at the temperature of the electric arc [1] to form acetylene which was necessarily accompanied by some methane and ethane resulting from the pyrogenetic decomposition of the acetylene.

Bone and Jerdan state that carbon unites directly with hydrogen at 1200° forming 1 to 2% *methane.*[2]

But Berthelot, carrying out the reaction with pure carbon in a quartz tube, could not confirm the formation of methane and concluded that it must have come from impurities in the carbon used by the English chemists.[3]

[1] BERTHELOT, *Ann. Chim. Phys.* (4), **13**, 143 (1868).
[2] BONE and JERDAN, *J. Chem. Soc.*, **71**, 42 (1897).
[3] BERTHELOT, *Ann. Chim. Phys* (8), **6**, 183 (1905).

410. According to Henseling, the formation of methane by carbon and hydrogen begins at 300° in the presence of finely divided nickel.

Sabatier and Senderens, by passing hydrogen at 250° over the intimate mixture of carbon and nickel which is formed by the action of reduced nickel on carbon monoxide between 250 and 300°, have definitely proved the production of methane, but also detected water vapor. After some time the formation of methane ceased though there was still much carbon with the metal. They attributed the formation of methane and water to the presence of a nickel carbonyl combination formed by the action of the carbon monoxide. The same chemists found no methane when the carbonaceous mixture had been prepared above 400°, a temperature at which carbonyl compounds can not exist.[4]

411. Mayer and Altmayer have confirmed the *very slow* formation of methane from carbon in contact with nickel or cobalt. At all temperatures above 250° methane is decomposed by nickel into carbon and hydrogen, the amount remaining being fixed for each temperature, and the same whether the limit be approached from above or from below as is true with all reversible reactions (19), and not altered when cobalt is substituted for nickel. The amounts of methane at equilibrium are:

At 250° .... 98.8% by volume
    536° 51.2%
    625° 24.7%
    850° 1.6%

But this formation is very slow and could never be used for the preparation of methane. The velocities of the mixtures of gases passed over the mixture of carbon and nickel to obtain the equilibrium were not over 0.2 to 0.3 cc. per minute.[5]

2. Ethylene Double Bond

412. The ethylene double bond is very easily attacked by direct hydrogenation over nickel and adds two atoms of hydrogen. This is readily accomplished by nickel reduced above 500° and even by nickel which has been weakened by the action of poisons.

413. Hydrocarbons. *Ethylene* is hydrogenated by nickel from 30° up, the reaction which continues indefinitely, with evolution of heat, gives ethane exclusively. The hydrogenation is more rapid toward 130–150°.[6]

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[4] Sabatier and Senderens, *Bull. Soc. Chim.* (4), **1**, 107 (1907).

[5] Mayer and Altmayer, *Berichte*, **40**, 2134 (1907).

[6] Sabatier and Senderens, *Compt. rend.*, **124**, 1359 (1897).

In the presence of excess of hydrogen, all the ethylene disappears, while with excess of ethylene all the hydrogen is used up and a mixture of ethane and ethylene is obtained from which it is easy to remove the latter by bromine water leaving the ethane pure.

This reaction has been used for the manufacture of *ethane* for refrigerating machines. The mixture of equal volumes of ethylene and hydrogen is passed through tubes 1 m. long and 7.5 cm. in diameter containing reduced nickel and heated to 200°. With a velocity of 2 cu. m. per hour a gas containing 80% of ethane is obtained. In order to complete the union of hydrogen and ethylene the mixture is compressed to 30 or 40 atmospheres in a vessel filled with nickeled pumice.[7]

Above 300° nickel decomposes ethylene (912) with the liberation of carbon, and the production of methane and certain amounts of higher paraffines which can be liquefied.[6]

414. Other ethylene hydrocarbons can be transformed into the corresponding *saturated hydrocarbons* below 160° without any complications. But above 200° and particularly above 300° there can be partial breaking of the carbon chain with the formation of saturated hydrocarbons with smaller numbers of carbon atoms and also more complicated.

With *propylene,* $CH_3.CH:CH_2$, the reaction commences in the cold and up to 200° nothing but *propane,* $CH_3 . CH_2 . CH_3$, is produced so long as the hydrogen is in slight excess. When the propylene is in excess, particularly above 290°, small amounts of higher liquid hydrocarbons with petroleum odors are formed, and at higher temperatures there is more and more deposition of carbon with splitting up of the propane.

Trimethyl-ethylene, or *2-methyl-butylene,* $(CH_3)_2C : CH . CH_3$, is totally hydrogenated by excess of hydrogen into pure *2-methylbutane* or *isopentane,* at 150°.

Likewise *hexene* (2) gives *hexane;* and *caprylene,* or *octene* (1), *octane* without complications below 160°.[8]

By the hydrogenation of 2,2-*dimethyl-methylene* (3)-*pentane,* over nickel at 160°, 2,2,3-*trimethyl-pentane,* boiling at 110.5° is obtained, and likewise 2,5-*dimethyl-heptane,* boiling at 135° from 2-*ethyl-5-methyl-hexene.*[9]

[6] Sabatier and Senderens, *Compt. Rend.,* **124,** 1359 (1897).

[7] Sprent, *J. Soc. Chem. Ind.,* **32,** 171 (1913).

[8] Sabatier and Senderens, *Compt. rend.,* **134,** 1127 (1902).

[9] Clark and Jones, *J. Amer. Chem. Soc.,* **34,** 170 (1912). Clark and Beggs, *Ibid.,* **34,** 54 (1912).

Likewise *nonene*(2) is transformed entirely into *nonane*.[10]

Methyl-propyl-octene gives the corresponding *methyl-propyl-octane, and* 4-*cyclohexyl-heptene,* the 4-*cyclohexyl-heptane.*[11]

415. In the case of phenyl- or polyphenyl-ethylene hydrocarbons, when the hydrogenation is carried out with a weakened nickel such as is not capable of hydrogenating benzene (56), or with active nickel at 300°, the aliphatic double bonds are saturated without hydrogenating the aromatic nuclei.

Thus *styrene,* $C_6H_5 . CH : CH_2$, gives only *ethyl-benzene,* $C_6H_5 . CH_2CH_3$.

The *ortho, meta,* and *para, cresyl-propenes*(2) are regularly changed into the *ortho, meta,* and *para cymenes.*[12]

1-*Phenyl-2-propyl-pentene* yields 1-*phenyl-2-propyl-pentane.*[11]

Stilbene, or symmetrical diphenyl ethylene, $C_6H_5.CH:CH.C_6H_5$, is readily transformed by a slightly active nickel at 240° into *dibenzyl,* $C_6H_5.CH_2.CH_2.C_6H_5$. Likewise $\alpha\alpha$-*Diphenyl-ethylene* is readily changed to $\alpha\alpha$-*diphenyl-ethane,* 1,2-*diphenyl-propene*(1) and 1,1-*diphenyl-propene*(2) furnish the corresponding *diphenyl-propanes* and similar statements hold for the *diphenyl-butenes* and *diphenyl-pentenes.*[13]

Ocimene, $(CH_3)_2C:CH.CH_2.CH:C.CH:CH_2$, or 2,6-*dimethyl-octa-*
$$\overset{\cdot}{C}H_3$$
triene(2,5,7), of oil of basil is readily hydrogenated over nickel at 130–140° to the corresponding 2,6-dimethyl-octane boiling at 158°.[14]

416. **Unsaturated Alcohols.** The fixation of hydrogen frequently takes place without alteration of the alcohol group.

Propenol, or *allyl alcohol,* $CH_2 : CH . CH_2OH$, is readily hydrogenated at 130–170° over nickel, to give nearly pure *propyl alcohol* containing only a slight amount of propionic aldehyde.[15]

Geraniol, $(CH_3)_2C:CH.CH_2.CH_2.C:CH.CH_2OH$, or 2,6-*dimethyl-*
$$\overset{\cdot}{C}H_3$$
octadiene(2,6)*ol*(8), is readily hydrogenated at 130–140° to give the corresponding *dimethyl-octanol.* At the same time a little of it is reduced to the saturated hydrocarbon.

[10] CLARK and JONES, *J. Amer. Chem. Soc.,* **37,** 2536 (1915).
[11] MURAT and AMOUROUX, *J. Pharm. Chim.* (7), **5,** 473 (1912), *C. A.,* **7,** 1494.
[12] SABATIER and MURAT, *Compt. rend.,* **156,** 184 (1913).
[13] SABATIER and MURAT, *Ann. Chim.* (9), **4,** 284–297 (1915).
[14] ENKLAAR, *Berichte,* **41,** 2085 (1908).
[15] SABATIER, *Compt. rend.,* **144,** 879 (1907).

The hydrogenation of *linalool, or* 2,6-*dimethyl-octadiene*(2,7)-*ol*(6), $(CH_3)_2C : CH . CH_2 . CH_2 . C(OH) . CH : CH_2$, furnishes the

$$CH_3$$

same products.[16]

Citronellol, $(CH_3)_2C : CH . CH_2 . CH_2 . CH . CH_2 . CH_2OH$, like-

$$\dot{C}H_3$$

wise gives *dihydrocitronellol.*[17]

We have seen (208) that the hydrogenation, over nickel at 200°, of secondary α-unsaturated alcohols gives the isomeric saturated ketone instead of the saturated secondary alcohol, by a simple migration of the hydrogen of the alcohol group.

417. Esters. The esters of *unsaturated acids* are readily hydrogenated over nickel whatever be the position of the double bond.

Esters of *acrylic acid* give esters of *propionic* at 180°.

Ethyl dimethyl-acrylate likewise gives *ethyl isovalerate,* and *ethyl undecylenate,* the *undecylate.*

It is the same way with ethyl *œnanthylidene-acetate,* $C_6H_{13}.-CH : CH . CO_2 . C_2H_5$.

The same fixation of hydrogen takes place with the esters of unsaturated aromatic acids without the hydrogenation of the nucleus. *Methyl cinnamate,* $C_6H_5 . CH : CH . CO_2 . CH_3$, gives *methyl phenylpropionate.*

Ethyl phenyl-isocrotonate, $C_6H_5 . CH : CH . CH_2 . CO_2 . C_2H_5$, acts in a similar manner.[18]

418. Ethers of Unsaturated Alcohols. The vapors of *allyl ether,* carried by an excess of hydrogen over nickel at 138–140° are totally changed to *propyl ether.*[19]

Isosafrol, $CH_3.CH : CH.C_6H_3\overset{\displaystyle O}{\underset{\displaystyle O}{\diamondsuit}}CH_2$, is hydrogenated in

the side chain to *dihydrosafrol* without affecting the ether group.[20]

419. Unsaturated Aldehydes. *Acroleïne,* $CH_2 : CH . CHO$, is hydrogenated over nickel at 160° to *propionic aldehyde,*[21] which can be further hydrogenated, by a slower reaction, to propyl alcohol.

Likewise crotonic aldehyde over nickel at 125° is changed to buty-

[16] ENKLAAR, *Rec. Trav. Chim. Pays-Bas,* **27,** 411 (1908), and *Berichte,* 41, 2085 (1908).

[17] HALLER and MARTINE, *Compt. rend.,* **140,** 1303 (1905).

[18] DARZENS, *Compt. rend.,* **144,** 328 (1907).

[19] SABATIER, *Compt. rend.,* **144,** 879 (1907).

[20] HENRARD, *Ch. Wkbld.,* **4,** 630–2; *Chem. Cent.,* **1907** (2), 1512.

[21] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 399 (1905).

ric aldehyde with a yield of 50%, with about 20% of butyl alcohol resulting from the subsequent hydrogenation of the aldehyde.[22]

420. Unsaturated Ketones. The fixation of hydrogen on ethylene double bonds is so rapid that it can be effected before the ketone group, $-CO-$, is changed to the secondary alcohol group, $-CH(OH)-$.

Mesityl oxide, $(CH_3)_2C : CH . CO . CH_3$, is transformed at 160–170° into 2–*methyl-pentanone*(4),[23] accompanied by some of the corresponding alcohol and even of *isopentane*.[24] Likewise *methyl-hexenone*, $(CH_3)_2C : CH . CH_2 . CO . CH_3$, gives the corresponding *methyl-hexanone*.

3–*Methyl-heptene*(3)*one*(5) is transformed at 180° into 3–*methyl-heptanone*(5), and likewise 2,4,8–*trimethyl-nonene*(4)*one*(6) gives the corresponding saturated ketone.[25]

Phorone, $(CH_3)_2C : CH . CO . CH : C(CH_3)_2$, when hydrogenated over nickel at 160–170°, is totally changed to *di-isobutyl-ketone*, or *isovalerone*.[26] By operating at 225° the ketone is accompanied by the alcohol and the saturated hydrocarbon.[27]

421. By hydrogenating *pulegone* rapidly over nickel at 140–160°, the unsaturated side chain can be hydrogenated without affecting the ketone group to give *pulegomenthone:* [28]

$$(CH_3)_2C : C\begin{array}{c} CO.CH_2 \\ CH_2.CH_2 \end{array} CH.CH_3 \rightarrow (CH_3)_2CH.CH\begin{array}{c} CO.CH_2 \\ CH_2.CH_2 \end{array} CH.CH_3.$$

$$Camphorone, \quad CH_3.CH\begin{array}{c} CO \\ CH_2.CH_2 \end{array}C : C(CH_3)_2 \quad \text{is hydrogenated}$$
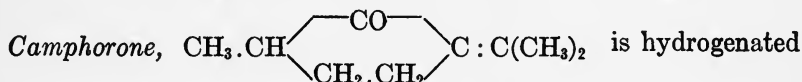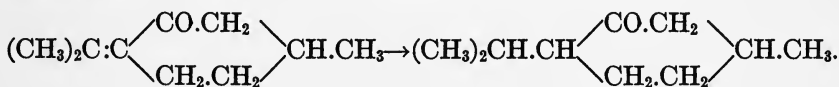
over nickel at 130° to give *dihydrocamphorone*, boiling at 182°.[29]

422. Unsaturated Acids. Their hydrogenation is readily carried out over nickel without any damage to the catalytic metal. The vapors of *crotonic acid*, $CH_3 . CH : CH . COOH$, at 190° give butyric acid quantitatively. The vapors of *oleïc acid*, carried along by a violent current of hydrogen over nickel at 280–300°, are readily transformed into solid *stearic acid*, and the same is true of its isomer *elaïdic acid*.[30]

[22] Douris, *Bull. Soc. Chim.* (4), **9**, 922 (1911).

[23] Darzens, *Compt. rend.*, **140**, 152 (1905).

[24] Skita, *Berichte*, **41**, 2938 (1908).

[25] Bodroux and Taboury, *Compt. rend.*, **149**, 422 (1909).

[26] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **16**, 79 (1909).

[27] Skita, *Loc. cit.*

[28] Haller and Martine, *Compt. rend.*, **140**, 1298 (1905).

[29] Godchot and Taboury, *Compt. rend.*, **156**, 470 (1913).

[30] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **16**, 73 (1909).

3. The Acetylene Triple Bond

423. If hydrogen mixed with a small proportion of acetylene is passed over cold reduced nickel, the metal becomes warm, the more so when the proportion of acetylene is increased. With 2 volumes of hydrogen to 1 of acetylene the spontaneous evolution of heat may heat the end of the nickel train to 150°. The contraction of the gas is enormous, greater than corresponds to the formation of ethane:

$$C_2H_2 + 2H_2 = C_2H_6.$$

The volume is reduced to one fourth, although a little unchanged acetylene and some *ethylene* remain, showing incomplete hydrogenation, because there is produced at the same time a considerable proportion of higher hydrocarbons, part of which are liquefied. The nickel is coated with a little carbon which is readily separated by dilute acids.

On the contrary, the formation of ethane is complete in the presence of an excess of hydrogen.

424. Inversely if the proportion of acetylene in the mixture is increased, the metal heats up more, the liquids formed become more abundant and the presence of hydroaromatic and aromatic hydrocarbons can be shown. Finally, an incandescence is noticed similar to that produced by acetylene alone on nickel (914).[31]

425. *α-Heptine*, or *œnanthylidene*, is readily hydrogenated over nickel to *n.heptane*.[32]

4. The Triple Bond Between Carbon and Nitrogen

426. The direct hydrogenation of *nitriles*, $R.C \vdots N$, easily carried out with nickel, leads to the formation of the primary amines, $R.CH_2.NH_2$, which on account of secondary reactions caused by the metal, are accompanied by secondary and tertiary amines. These reactions correspond to the formation of ammonia which is eliminated, and consequently the *secondary amine* constitutes the major portion of the product. We have:

$$2 \underline{R.CH_2.NH_2} = NH_3 + \underline{(R.CH_2)_2NH}$$
$$\text{\footnotesize primary amine} \qquad\qquad \text{\footnotesize secondary amine}$$

and $R.CH_2.NH_2 + (R.CH_2)_2NH = NH_3 + \underline{(R.CH_2)_3N.}$
$$\text{\footnotesize tertiary amine}$$
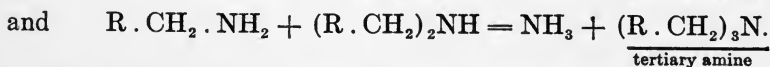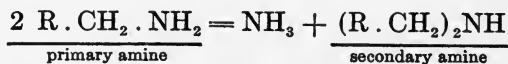
427. Aliphatic Nitriles. *Formic-nitrile* or *hydrocyanic acid* is not

[31] Sabatier and Senderens, *Compt. rend.*, **128**, 1173 (1899).
[32] Sabatier and Senderens, *Compt. rend.*, **135**, 87 (1902).

affected by hydrogenation except above 250° but then gives the three methyl-amines and ammonia.

Acetonitrile is readily hydrogenated at 200° and gives a mixture containing 60% *diethyl-amine,* and 20% each of the *mono-* and *tri-*amines.

With *ethyl cyanide,* the *dipropyl-amine* forms nearly 80% of the product.

Isoamyl cyanide likewise gives chiefly secondary amine, the primary being formed in least amount. The amines are accompanied by a little isopentane.

It is evident that the hydrogenation of aliphatic nitriles gives us a valuable and convenient method of preparing secondary amines.[33]

428. Aromatic Nitriles. The results are not nearly as good with aromatic nitriles from which the hydrocarbons and ammonia are formed.

However, the hydrogenation of *benzonitrile* at 250° gives a certain proportion of *benzyl-amine* and *dibenzyl-amine* and the same is true of *p.toluo-nitrile* which gives a mixture of the primary and secondary amines.[34]

429. Dicyanides. *Ethylene dicyanide,* when hydrogenated over nickel, gives a certain proportion of *tetramethylene-diamine* resulting from the regular hydrogenation:

$$CN . CH_2 . CH_2 . CN + 4H_2 = NH_2 . CH_2 . CH_2 . CH_2 . CH_2 . NH_2.$$

This is accompanied by a little ammonia and *pyrrolidine,*

$$\begin{array}{c} CH_2 . CH_2 \\ \cdot \qquad\qquad \diagdown NH, \\ CH_2 . CH_2 \diagup \end{array}$$ resulting from its decomposition.[35]
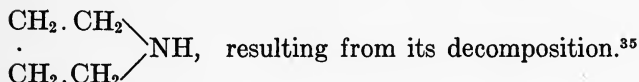
5. Quadruple Bond Between Carbon and Nitrogen

430. Carbylamines. The aliphatic *isocyanides,* or *carbylamines,* $R . N \vdots C$, which former wet reduction methods were unable to hydrogenate because they were decomposed by hydration, can add 4H over nickel at 160–180° to form the *secondary amines,* $R . NH . CH_3$

They are accompanied by a small amount of the primary amine, $R . CH_2 . NH_2$, and the secondary amine, $(R . CH_2)_2NH$, resulting from the hydrogenation of the nitrile, $R . C \vdots N$, produced by partial isomerization of the isocyanide.

Methyl carbylamine gives a yield of 80% of *dimethyl-amine.*

[33] SABATIER and SENDERENS, *Compt. rend.,* **140**, 482 (1905).

[34] FRÉBAULT, *Compt. rend.,* **140**, 1036 (1905).

[35] GAUDION, *Bull. Soc. Chim.* (4), **7**, 824 (1910).

The metal is gradually coated with tarry material which diminishes its activity.

Ethyl carbylamine gives chiefly *methyl-ethyl-amine* with a little mono- and di-propyl amines.

Tertiary-butyl-isocyanide, $(CH_3)_3C . N \vdots C$, hydrogenated at 170–180°, gives *methyl-tert.butyl-amine*, which has never been obtained by other methods.

If the reaction is carried on at 220–250°, the secondary amine molecule is broken up with the formation of ammonia and hydrocarbon.[36]

431. Aliphatic Carbimides. It is convenient to consider along with the carbylamines the *aliphatic carbimides*, or *isocyanates*, $R . N : CO$ (although the hydrogenation is not simply the addition of hydrogen but also its substitution for the oxygen atom), because the result is the same for both classes.

Over nickel at 180–190°, the chief reaction is:

$$R . N : CO + 3H_2 = H_2O + R . NH . CH_3.$$
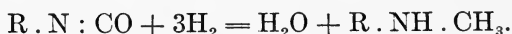
But a disturbance is caused by the water produced which reacts immediately with a part of the carbimide to form a disubstituted urea, $(R . NH)_2CO$, and carbon dioxide. The alkyl urea is immediately hydrogenated, giving:

$$(R . NH)_2CO + 3H_2 = H_2O + NH_2 . R + R . NH . CH_3.$$
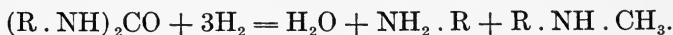
Hence there is a certain amount of the primary amine, $R . NH_2$, and on account of secondary actions of the metal, the secondary, R_2NH, and tertiary, R_3N, also.

Thus *ethyl isocyanate* gives a considerable amount of *methyl-ethyl-amine*, a little *diethyl-amine*, and traces of *ethyl-amine* and *triethyl-amine*.[37]

6. Double Bond between Carbon and Oxygen

432. The *carbonyl group*, CO, which frequently occurs in organic compounds, is readily hydrogenated over nickel to the alcohol group, CHOH.

Aliphatic Aldehydes. Hydrogenated over nickel below 180°, these are regularly transformed into the primary alcohols without the production of di-secondary glycols or acetals as by-products.

Formaldehyde vapors at 90° are readily transformed and *methyl*

[36] Sabatier and Mailhe, *Compt. rend.*, **144**, 955 (1907).
[37] Sabatier and Mailhe, *Compt. rend.*, **144**, 824 (1907).

alcohol is condensed along with water which is due to the formation of methane according to the reaction:

$$H . CO . H + 2H_2 = CH_4 + H_2O.$$

But the covering over of the metal surface with a thin coating of *trioxy-methylene* soon suppresses its activity. If the temperature is raised, this trouble disappears, but the formation of methane increases as well as the decomposition of the formaldehyde itself (508).

Acetaldehyde is readily transformed into alcohol around 140°, but at 200° the destruction of the aldehyde is already apparent.

Propionaldehyde is regularly hydrogenated to *propyl alcohol* between 100 and 145°.

It is the same with *isobutyric* and *isovaleric aldehydes* at 135–160° which yield about 70% of the alcohols, the rest of the product being unchanged aldehyde with a little acetal.

433. Aromatic Aldehydes. These do not give this reaction but tend to form the hydrocarbons; thus benzaldehyde at 210–235° gives *benzene* and *toluene* accompanied by a certain proportion of the corresponding cyclohexane compounds. The reaction which takes place is:

$$C_6H_5 . CHO + 2H_2 = C_6H_5 . CH_3 + H_2O$$
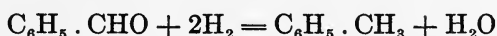
along with the decomposition of benzaldehyde by nickel:

$$C_6H_5 . CO . H = C_6H_6 + CO$$
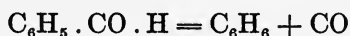
followed by a partial hydrogenation of the carbon monoxide to methane.[38]

434. Pyromucic Aldehyde. *Furfural,* or pyromucic aldehyde, $C_4H_3O . CHO$, hydrogenated over nickel at 190°, gives *furfuryl alcohol,* $C_4H_3O . CH_2OH$, accompanied by some secondary products (see 371 and 487).[39]

435. Aliphatic Ketones. Aliphatic ketones, being more stable towards nickel than the aldehydes, are hydrogenated regularly into the *secondary alcohols* and, unlike their conduct in the classic reduction by sodium amalgam, they do not form any secondary products such as pinacones. The method is an excellent one for the preparation of many secondary alcohols, which are produced almost quantitatively.

This process is readily applied to *acetone* which forms *isopropyl alcohol* at 115–125° which is thus prepared quite cheaply. It is no less good for *butanone,   diethyl-ketone,   methyl-isopropyl-ketone,*

[38] Sabatier and Senderens, *Compt. rend.,* **137**, 301 (1903).

[39] Padoa and Ponti, *Lincei,* **15** (2), 610 (1906), *C.,* 1907 (1), 570.

methyl-propyl-ketone, and *methyl-butyl-ketone.* It is only above 200° that decompositions of the molecules begin to take place.[40]

Diisopropyl[41] and *diisobutyl*[42] *ketones* are readily transformed into the secondary alcohols under the same conditions.

When the hydrogenation of ketones is carried out above 200° different results are obtained. *Acetone* hydrogenated between 200 and 300° gives neither isopropyl alcohol nor its pinacone, but chiefly methyl-isobutyl-ketone (boiling at 114°) accompanied by diisobutyl-ketone (b . 165°).[43]

Methyl-nonyl-ketone, hydrogenated at 300°, does not give the corresponding alcohol but various products, one of them a ketone, $C_{22}H_{44}O$. [44]

436. Alicyclic Ketones. The method is readily applied to these.

Cyclopentanone is hydrogenated over nickel at 125° to give 50% of *cyclopentanol,* a little cyclopentane, and 40% of a complex ketone formed by the joining of two rings, the *cyclopentyl-cyclopentanone.*[45]

The α- and β-*methylcyclopentanones* are hydrogenated at 150° to the corresponding alcohols, accompanied by greater quantities of the *dimethylcyclopentyl-pentanones* formed by the union of two rings.[46]

Cyclohexanone and the three methyl-cyclohexanones are regularly hydrogenated below 180° to the corresponding alcohols with small amounts of the hydrocarbons.[47]
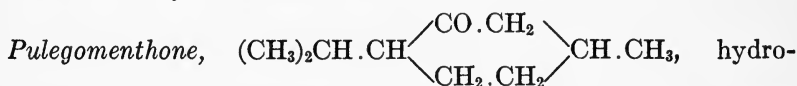
Pulegomenthone, $(CH_3)_2CH.CH{\overset{\displaystyle CO.CH_2}{\underset{\displaystyle CH_2.CH_2}{\Big<}}\Big>}CH.CH_3$,   hydro-

genated by an active nickel at 140–160°, gives a mixture of *menthol* and *pulegomenthol.*[48]

437. Keto-acids. *Laevulinic* acid, $CH_3.CO.CH_2.CH_2.COOH$, hydrogenated over nickel around 250°, gives the hydroxy-acid, which loses water to form *valerolactone,* $CH_3.CH.CH_2.CH_2.CO.$[49]
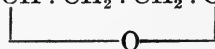
438. Diketones. The results of the hydrogenation of these depend on the nature of the compounds.[50]

[40] Sabatier and Senderens, *Compt. rend.,* **137,** 302 (1903).
[41] Amouroux, *Bull. Soc. Chim.* (4), **7,** 154 (1910).
[42] Mailhe, *Bull. Soc. Chim.* (4), **15,** 327 (1914).
[43] Lassieur, *Compt. rend.,* **156,** 795 (1913).
[44] Haller and Lassieur, *Compt. rend.,* **150,** 1017 (1910).
[45] Godchot and Taboury, *Compt. rend.,* **152,** 881 (1911).
[46] Godchot and Taboury, *Bull. Soc. Chim.* (4), **13,** 591 (1913).
[47] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4,** 402 (1905).
[48] Haller and Martine, *Compt. rend.,* **140,** 1298 (1905).
[49] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **16,** 78 (1909).
[50] Sabatier and Mailhe, *Compt. rend.,* **144,** 1086 (1907).

α-Aliphatic Diketones. Diacetyl, or *butanedione,* $CH_3.CO.-CO.CH_3$, by hydrogenation at 140–150°, is totally transformed into a mixture of *butanol-one* (2,3), $CH_3.CH(OH).CO.CH_3$, and butanediol (2,3), $CH_3.CH(OH).CH(OH).CH_3$.

439. *β-Aliphatic Diketones. Acetyl-acetone,* $CH_3.CO.CH_2.-CO.CH_3$, when hydrogenated at 150°, gives two simultaneous reactions. One part is normally hydrogenated to form *pentol* (2) *one* (4), $CH_3.CH(OH).CH_2.CO.CH_3$, while the larger portion is split into two fragments:

$$CH_3.CO.CH_2.CO.CH_3 + H_2 = CH_3.CO.H + CH_3.CO.CH_3.$$
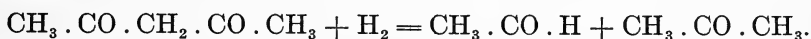
The acetaldehyde and acetone thus formed are then reduced to *ethyl* and *isopropyl alcohols.*

Methyl-acetyl-acetone, $CH_3.CO.CH(CH_3).CO.CH_3$, forms hardly anything but the decomposition products.

440. *γ-Aliphatic Diketones. Acetonyl-acetone,* $CH_3.CO.CH_2.-CH_2.CO.CH_3$, when hydrogenated at 190°, is totally transformed, not into the corresponding *diol* but into the *ether,* $CH_3.CH.CH_2.CH_2.CH.CH_3$, produced by its dehydration.

$\overline{}O\overline{}$
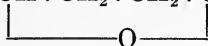
441. Aromatic Ketones. Aromatic ketones and diketones give the corresponding alcohols by hydrogenation but go chiefly into the hydrocarbons (389 *et seq.*).

442. Quinones. We can consider *quinones* as unsaturated alicyclic diketones. They are readily hydrogenated by nickel at 200°, and add H_2 to form the corresponding *diphenols* in excellent yields.

This is the case with ordinary *quinone* which gives *hydroquinone* quantitatively, with *toluquinone,* with *p.xyloquinone,* and with *thymoquinone.*

But if the operation is carried on at a higher temperature, 220 to 250°, the diphenol is no longer obtained, but water, the monophenol, and even the hydrocarbon.[51]

443. Ethylene Oxides. The direct hydrogenation of these *oxides* is doubtless readily carried out in all cases.

In the particular case of the ether of *cyclohexanediol* (1,2), hydrogen is added at 160° to give a quantitative yield of *cyclohexanol:* [52]

$$\begin{matrix} CH_2.CH_2.CH \\ . \qquad . \qquad \diagdown \\ \qquad \qquad \qquad >O \\ . \qquad . \qquad \diagup \\ CH_2.CH_2.CH \end{matrix} \rightarrow \begin{matrix} CH_2.CH_2.CHOH \\ . \qquad . \\ . \qquad . \\ CH_2.CH_2.CH_2 \end{matrix}$$
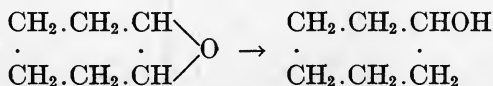
[51] SABATIER and MAILHE, *Compt. rend.,* **146**, 457 (1908).
[52] BRUNEL, *Ann. Chim. Phys.* (8), **6**, 237 (1905).

7. The Aromatic Nucleus

444. The direct hydrogenation of the aromatic nucleus has long been considered very difficult to accomplish. When benzene is reduced by concentrated hydriodic acid at 250°, *cyclohexane*, C_6H_{12}, is not produced as was hoped, but its isomer, *methyl-pentamethylene*, boiling at 69°, is formed by a molecular rearrangement.[53] However, this method of reduction has been successfully used with *toluene* and *m.xylene* which give certain amounts of the corresponding saturated cyclic compounds. But this formation is very difficult and most of the aromatic hydrocarbons can not be hydrogenated in this way. The hydroaromatic hydrocarbons might be separated from Baku petroleum by laborious fractionations or prepared by tedious synthetic processes.

The direct hydrogenation of phenol and of its homologs had never been accomplished, nor had that of aniline and related aromatic amines.

On the contrary, benzoic and the phthalic acids had been hydrogenated by sodium amalgam.

445. In 1900, Lunge and Akunoff showed that combination takes place when a mixture of benzene vapor and hydrogen is passed over *platinum black* in the cold, or better, at 100°, and calculated from the decrease in volume of the mixture that *cyclohexane*, C_6H_{12}, must have been formed although the same reaction with *platinum sponge* gave only *cyclohexene*, C_6H_{10}. But the activity of the catalyst was quickly exhausted, and they were not able to isolate any product of the hydrogenation.[54]

The use of reduced nickel enables us to hydrogenate the aromatic nucleus regularly in most cases. This hydrogenation ordinarily takes place around 180° without isomerization and usually without side reactions, hence with good yields. This is without doubt the most important service rendered by reduced nickel.

446. **Aromatic Hydrocarbons.** The direct hydrogenation of *benzene* to cyclohexane, C_6H_{12}, takes place with nickel above 70°. Its speed increases with the temperature up to 170–190°, where it is rapid without any side reaction. Above that, and particularly above 300°, a part of the benzene is reduced to methane and carbon is deposited on the nickel.

Cyclohexane is sometimes obtained at once, but usually it contains some benzene which has escaped the reaction and which is more

[53] KISHNER, *J. prakt. Chem.* (2), **56**, 364 (1897).
[54] LUNGE and AKUNOFF, *Zeit. anorgan. Chem.*, **24**, 191 (1900).

abundant the more worn out the nickel is. Treatment with a mixture of 1 volume fuming nitric acid to 2 volumes concentrated sulphuric acid easily removes the benzene.[55]

447. All of the homologs of benzene are hydrogenated over nickel at 150 to 180°, being transformed into the homologs of cyclohexane.

Below 250° the hydrogenation takes place without any complications with the methyl derivatives of benzene, *toluene, ortho, meta,* and *para xylene, mesitylene* and *pseudocumene,* the yields of the corresponding methyl cyclohexane derivatives being practically quantitative, though traces of the aromatic hydrocarbons remain. These may be readily eliminated by shaking with the nitric-sulphuric acid mixture which has little effect on the saturated hydrocarbons in the cold.

448. But if we start with substituted benzenes containing long side chains, ethyl, propyl, isopropyl, and butyl, while the corresponding derivative of cyclohexane is always the chief product, there is always more or less of the saturated hydrocarbon resulting from the shortening of the long side chain. Thus *ethyl-benzene* gives, along with *ethyl-cyclohexane,* a little *methyl-cyclohexane* with correlative formation of methane. *Propyl-benzene* gives a little ethyl- and methyl-cyclohexane. This disturbance is more serious when the long side chain is a branched one, *e. g., isopropyl.* Thus with p.cymene which is *p.methyl-isopropyl-benzene,* along with about 66% of *p.methyl-isopropyl-cyclohexane,* about 16% each of *p.dimethyl-* and *p.methyl-ethyl-cyclohexane* are obtained.

This formation of by-products which is due to the power that the nickel has of dissociating the molecules, is greater with higher temperature, and for that reason it is best not to go above 180°.

449. By this method, *methyl-cyclohexane,* the three *dimethyl-cyclohexanes,* 1,3,5– and 1,3,4–*trimethyl-cyclohexanes, propyl-cyclohexane, p.methyl-ethyl-cyclohexane, isopropyl-cyclohexane,* the three *methyl-isopropyl-cyclohexanes* or *menthanes,* and *dimethyl-isobutyl-cyclohexane* have been prepared.[56]

450. Above 250°, and particularly above 300°, the production of the cyclohexane hydrocarbons diminishes and then disappears altogether since the inverse dehydrogenation begins and becomes more and more rapid (641).

451. *Phenyl-ethylene, styrene,* or *cinnamine,* $C_6H_5 . CH : CH_2$, is

[55] SABATIER and SENDERENS, *Compt. rend.,* **132,** 210 (1901).

[56] SABATIER and SENDERENS, *Compt. rend.,* **132,** 566 and 1254 (1901). SABATIER and MURAT, *Compt. rend.,* **156,** 184 (1913), and *Ann. Chim.* (9), **4,** 271 (1915).

hydrogenated at 160° by an active nickel to *ethyl-cyclohexane*. With a slightly active nickel around 200° hardly anything but *ethyl-benzene* is obtained.[57]

Phenyl-acetylene, $C_6H_5 . C \vdots CH$, hydrogenated over nickel at 180°, gives almost exclusively *ethyl-cyclohexane*.[58]

452. Polycyclic Aromatic Hydrocarbons. Hydrogenation over active nickel at about 170° permits the addition of 6 atoms of hydrogen to each aromatic nucleus. The low volatility of the polyphenyl hydrocarbons, which do not boil except at temperatures above 250°, makes it necessary to carry their vapors along by a large excess of hydrogen. A single passage over the nickel under the conditions used for benzene does not effect complete hydrogenation and it is usually necessary to repeat the process with the product.

However, a single operation is all that is required to transform diphenyl-methane, $C_6H_5 . CH_2 . C_6H_5$, into *dicyclohexyl-methane*, $C_6H_{11} . CH_2 . C_6H_{11}$.[59]

With *diphenyl*, $C_6H_5 . C_6H_5$, Eijkman [59] obtained only *phenyl-cyclohexane*, $C_6H_5 . C_6H_{11}$, boiling at 240°, but Sabatier and Murat have succeeded in transforming it into *dicyclohexyl*, $C_6H_{11} . C_6H_{11}$, melting at 4° and boiling at 233° and almost unattacked by the mixture of nitric and sulphuric acids.[60]

Likewise symmetrical *diphenyl-ethane*, or *dibenzyl*, $C_6H_5 . CH_2 .- CH_2 . C_6H_5$, has been completely transformed into 1,2–*dicyclohexyl-ethane*, $C_6H_{11} . CH_2 . CH_2 . C_6H_{11}$, boiling at 270°. The 1,1–*diphenyl-ethane*, $(C_6H_5)_2CH . CH_3$, is changed with greater difficulty into the 1,1–*dicyclohexyl-ethane* boiling at 256°.

The four *diphenyl-propanes* are more or less readily transformed into the *dicyclohexyl-propanes* over nickel at around 170°.

Only in the case of *dimethyl-diphenyl-methane*, $(C_6H_5)_2C(CH_3)_2$, a quaternary hydrocarbon, is there any notable breaking up of the molecule into *isopropyl-cyclohexane*, *ethyl-cyclohexane*, *methyl-cyclohexane* and even *cyclohexane*.

Five *diphenyl-butanes* have been easily hydrogenated over active nickel at 170°, to the corresponding *dicyclohexyl-butanes*, and like results have been obtained with three *diphenyl-pentanes* which do not boil below about 300°.[61]

453. According to whether the temperature is higher or lower, *triphenyl-methane*, $CH(C_6H_5)_3$, gives first *dicyclohexyl-phenyl-*

[57] SABATIER and SENDERENS, *Compt. rend.*, **132**, 1255 (1901).

[58] SABATIER and SENDERENS, *Compt. rend.*, **135**, 88 (1902).

[59] EIJKMAN, *Chem. Weekblad*, **1**, 7 (1903), *C.*, 1903 (2), 989.

[60] SABATIER and MURAT, *Compt. rend.*, **154**, 1390 (1912).

[61] SABATIER and MURAT, *Ann. Chim.* (9), **4**, 303 (1915).

methane, $C_6H_5 \cdot CH(C_6H_{11})_2$, and then *tricyclohexyl-methane,* $CH(C_6H_{11})_3$.[62]

On the contrary, the hydrogenation of symmetrical *tetraphenyl-ethane,* $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$, has miscarried, since under the influence of very active nickel at 230–240°, it yields only *dicyclohexyl-methane* produced by the hydrogenation of the two halves of the molecule.[63]

454. *Hydrindene,* which can be regarded as benzene with a saturated side chain, $C_6H_4 \overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{\diagdown \diagup}} CH_2$, adds 6 atoms of hydrogen

to form *dicyclononane,* C_9H_{16}, boiling at 163°.[64]

Fluorene, $\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{\cdot \diagdown \diagup}} CH_2$, over nickel at 150°, furnishes only the

decahydro-fluorene boiling at 258°.[65]

455. Aromatic Ketones. With an active nickel at a moderate temperature, the –CO– group is changed to –CH_2– and the aromatic rings are hydrogenated (389).

Thus *acetophenone* gives *ethyl-cyclohexane.*

Dibenzyl-ketone, $C_6H_5 \cdot CH_2 \cdot CO \cdot CH_2 \cdot C_6H_5$, with active nickel at 175°,[66] can give immediately symmetrical *dicyclohexyl-propane,* $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_{11}$.

456. Phenols. The direct hydrogenation of the aromatic nucleus can be readily accomplished in phenol and its homologs by the use of nickel.

Phenol, hydrogenated at 180°, gives immediately *cyclohexanol,* $C_6H_{11} \cdot OH$, containing 5 to 10% unchanged phenol, small quantities *cyclohexanone* and *cyclohexene,* C_6H_{10}. The mixture boiling between 155 and 165° can be purified by a second passage over the nickel at 150–170° which changes the phenol and cyclohexanone completely into cyclohexanol.[67]

457. *o.Cresol* is regularly transformed by nickel at 200–220° into *o.methyl-cyclohexanol* with a yield of better than 90%. There is a little of the ketone which can be extracted with sodium bisulphite.

m.Cresol, under the same conditions, gives a mixture of the alcohol

[62] Godchot, *Compt. rend.,* **147,** 1057 (1908).

[63] Sabatier and Murat, *Compt. rend.,* **157,** 1497 (1913).

[64] Eijkman, *Chem. Weekblad,* **1,** 7 (1903), *C.,* **1903** (2), 989.

[65] Schmidt and Metzger, *Berichte,* **40,** 4566 (1907).

[66] Sabatier and Murat, *Compt. rend.,* **155,** 385 (1912).

[67] Sabatier and Senderens, *Compt. rend.,* **137,** 1025 (1903).

and ketone which can be rehydrogenated at 180° to give practically pure *m.methyl-cyclohexanol.*

p.Cresol is readily hydrogenated at 200–230° to form *p.methyl-cyclohexanol* containing only traces of the ketone which are readily eliminated by bisulphite.[68]

458. The *xylenols,* or *dimethyl-phenols,* are hydrogenated over nickel with varying degrees of success. 1,3–*Dimethyl-phenol*(4), at 190–200°, changes almost completely to the corresponding *dimethyl-cyclohexanol* with a little ketone and *m.*xylene.

The same may be said of the 1,4–*dimethyl-phenol*(2), which gives the corresponding *cyclohexanol* with about 10% of the ketone.

1,2–*Dimethyl-phenol*(4), hydrogenated under the same conditions, gives only about 25% of the desired *cyclohexanol,* about 8% of the ketone, while about 67% is reduced to *o.xylene.*[69]

459. In the same manner with an active nickel at below 160° the regular hydrogenation of *p.butyl-phenol,* *methyl-butyl-phenol,* one *dimethyl-butyl-phenol,*[70] and one *diethyl phenol*[71] have been hydrogenated into the corresponding cyclo-aliphatic alcohols.

Thymol is satisfactorily hydrogenated to *hexahydrothymol* at 180–185°.

The same may be said of its isomer *carvacrol,* which is hydrogenated at 195–200° to *hexahydrocarvacrol.*[72]

460. **Polyphenols.** The addition of 6H to the nucleus in polyphenols is difficult to realize by the use of nickel, doubtless because the desired reaction can be effected only between narrow temperature limits. At 200° the hydrogenation leads to phenol and benzene, mixed with cyclohexanol and cyclohexane, without any appreciable amount of the desired *cycloaliphatic* diols or triols.[73]

461. On the contrary, by lowering the temperature to around 130°, the normal addition of hydrogen can be accomplished in some cases.

Hydroquinone at 130°, gives exclusively *cyclohexadiol* (1,4), or *quinite,* as the *cis* form, but if the hydrogenation is carried on at 160°, a mixture of the *cis* and *trans* forms is obtained with some phenol and *cyclohexanol.*

Pyrocatechin, at 130°, gives exclusively *cyclohexadiol*(1,2), melting at 75°.

[68] Sabatier and Mailhe, *Compt. rend.,* **140,** 350 (1905).
[69] Sabatier and Mailhe, *Compt. rend.,* **142,** 553 (1906).
[70] Darzens and Rost, *Compt. rend.,* **152,** 607 (1911).
[71] Henderson and Boyd, *J. Chem. Soc.,* **99,** 2159 (1911).
[72] Brunel, *Compt. rend.,* **137,** 1268 (1903).
[73] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4,** 428 (1905).

Resorcine is difficult to hydrogenate at low temperatures on account of its slight volatility, but small amounts of *cyclohexadiol*(1,3), melting at 65°, have been isolated.[74]

462. *Pyrogallol*, at 120–130°, gives *cyclohexatriol*(1,2,3), melting at 67°.[74]

463. *Thymoquinol*, $C_3H_7(CH_3)C_6H_2(OH)_2$, is hydrogenated by nickel to *menthane-diol*(2,5), melting at 112°.[75]

464. **Ethers of Phenol.** By means of nickel, below 150°, we may accomplish the direct hydrogenation of phenol ethers without breaking up the molecules.

Thus *anisol*, $C_6H_5 . OCH_3$, gives *methoxy-cyclohexane*, $C_6H_{11} .- OCH_3$. The *methyl ethers* of the *cresols* are transformed into the corresponding *methoxy-methyl-cyclohexanols*. *Phenetol* gives *ethoxy-cyclohexanol*.[76]

465. **Aromatic Alcohols.** Up to the present, the hydrogenation over nickel has not been accomplished without eliminating the hydroxyl group. Thus *benzyl alcohol* gives *toluene* and *methyl-cyclohexane*.

p.Tolyl-dimethyl-carbinol, $CH_3 . C_6H_4 . C(OH)(CH_3)_2$, changes to *hexahydrocymene*, identical with menthane, when hydrogenated at 150°.[77]

466. **Aromatic Amines.** On hydrogenating *aniline* at 190°, ammonia is evolved and a nearly colorless liquid with strong ammoniacal odor is obtained which gives on fractionation:

1. A little benzene and cyclohexane, going over around 80°,
2. About 30% of *cyclohexyl-amine*, $C_6H_{11} . NH_2$, boiling at 134°,
3. A small amount of unchanged aniline, boiling at 182°,
4. A portion boiling above 190°, consisting of about 30% *dicyclohexyl-amine*, boiling at 252°, and about 30% of *cyclohexyl-aniline*, boiling at 279°, and a little *diphenyl-amine*, boiling at 311°.

The dicyclohexyl-amine comes from the decomposition of the cyclohexyl-amine by the nickel, with elimination of ammonia, similar to what has been mentioned in connection with the hydrogenation of nitriles (426). The cyclohexyl-aniline and the diphenyl-amine can be regarded as produced by the partial dehydrogenation of the dicyclohexyl-amine.[78]

[74] SABATIER and MAILHE, *Compt. rend.,* **146**, 1193 (1908).

[75] HENDERSON and SUTHERLAND, *J. Chem. Soc.,* **97**, 1616 (1910).

[76] BRUNEL, *Ann. Chim. Phys.* (8), **6**, 205 (1905). SABATIER and SENDERENS, *Bull. Soc. Chim.* (3), **33**, 616 (1905).

[77] SMIRNOV, *J. Russian Phys. Chem. Soc.,* **41**, 1374 (1909).

[78] SABATIER and SENDERENS, *Compt, rend.,* **138**, 457 (1906).

467. The *toluidines*, $CH_3 . C_6H_4 . NH_2$, are more difficult to hydrogenate than aniline, but appear to give similar results.

By operating with *m.toluidine* (boiling at 197°) over nickel at 200°, we obtain, along with a little *methyl-cyclohexane*, boiling at 101°, and unchanged *m.toluidine*, a considerable amount of *methocyclohexyl-amine*, $CH_3 . C_6H_{10} . NH_2$, boiling around 150° and having an intensely alkaline reaction, and higher alkaline products boiling at 145 and 175° respectively under 20 mm. pressure, which are doubtless *dimethocyclohexyl-amine* and *methocyclohexyl-aniline*. But the activity of the nickel falls off rapidly to nothing. This effect is even more marked with *ortho* and *para toluidines* and with the *xylidines*, whether these amines contain toxic substances or whether slightly volatile products of the reaction remain on the surface of the nickel and suppress its activity.[79]

468. The hydrogenation of the nucleus by nickel at 160–180° is more readily accomplished for anilines substituted in the NH_2- group. The most difficult of these is *methyl-aniline* which gives a rather moderate yield of *cyclohexyl-methyl-amine*. A secondary reaction, which becomes more and more important as the temperature is raised, tends to produce the aliphatic amine, with the simultaneous liberation of cyclohexane or benzene.

Much more satisfactory results are obtained with *ethyl-aniline*, which gives *cyclohexyl-ethyl-amine*, boiling at 164°, with *dimethylaniline*, which leads to *cyclohexyl-dimethyl-amine*, boiling at 165°, and with *diethyl-aniline* which yields *cyclohexyl-diethyl-amine*, boiling at 193°.[80]

469. *Diphenyl-amine*, $(C_6H_5)_2NH$, when submitted to hydrogenation over nickel at 250°, is decomposed into ammonia and cyclohexane. But by working at 190–210° with vapors of diphenyl-amine carried along by a large excess of hydrogen, it is possible to accomplish a regular hydrogenation, producing *cyclohexyl-aniline* and *dicyclohexylamine*, accompanied by certain amounts of cyclohexane, cyclohexylamine, and even aniline, resulting from the breaking up of the molecule by nickel.[81]

470. *Benzyl-amine*, such as is usually obtained by various methods of preparation, can not be hydrogenated over nickel without breaking up of the molecule into ammonia and toluene, even below 100°. The cause must be the presence of foreign substances which injure the catalyst, since the normal hydrogenation can be realized with

[79] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 387 (1905).

[80] SABATIER and SENDERENS, *Compt. rend.*, **138**, 1257 (1904).

[81] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 483 (1905).

benzyl-amine obtained by the catalytic action of thoria on a mixture of ammonia and benzyl alcohol vapors, and *hexahydrobenzyl-amine* is obtained, accompanied by *dihexahydrobenzyl-amine*.[82]

471. Aromatic Acids. Direct hydrogenation over nickel fails when it is applied to benzoic acid or its homologs. When the vapors of *benzoic acid,* carried along by an excess of hydrogen, are passed over a very active nickel at 180–200°, the production of a little cyclohexane and traces of hexahydrobenzoic acid is observed at the start, but after a very short time the benzoic acid passes on unchanged, the surface of the nickel having doubtless become coated with a stable benzoate.[83]

Sabatier and Senderens failed likewise in the hydrogenation of the *esters* of *benzoic acid,* as the nickel rapidly became inactive. But by operating with the metal block at a perfectly regulated temperature below 170°, Sabatier and Murat have succeeded in accomplishing the regular hydrogenation of *methyl benzoate,* and even more readily, the hydrogenation of the esters of higher alcohols, and have thus obtained *methyl, ethyl, isobutyl,* and *isoamyl hexahydrobenzoates,* the *isoamyl* ester in 80% yield. The saponification of these esters yields the *hexahydrobenzoic acid* immediately.[84]

By the same method, they realized the complete hydrogenation of esters of *phenyl-acetic* acid to those of *cyclohexyl-acetic* at 170–185°,[85] of esters of *hydrocinnamic* acid to esters of β-*cyclohexyl-propionic*,[86] and finally of esters of *ortho, meta,* and *para toluic* acids to those of the corresponding *hexahydrotoluic* acids.

8.   Various Ring Compounds

472. Trimethylene   Ring.   *Cyclopropane,* or   *trimethylene,*

$$CH_2\!\!\diagdown \atop CH_2\!\!\diagup \!\!CH_2,$$ is hydrogenated by nickel above 80°, and rapidly at 120°, to form *propane*.[87]

Likewise   *ethyl-trimethylene*   is hydrogenated   by   nickel   to *isopentane:*

$$\begin{array}{c} CH_2\diagdown \\ \cdot \quad \diagup CH.CH_2.CH_3 \\ CH_2 \end{array} \rightarrow \begin{array}{c} CH_3\diagdown \\ \diagup CH.CH_2.CH_3. \\ CH_3 \end{array}[88]$$
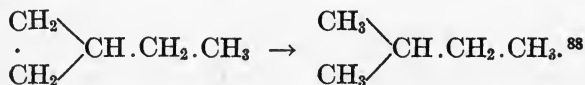
[82] SABATIER and MAILHE, *Compt. rend.,* **153,** 160 (1911).
[83] SABATIER and MURAT, *Compt. rend.,* **154,** 923 (1912).
[84] SABATIER and MURAT, *Compt. rend.,* **154,** 924 (1912).
[85] SABATIER and MURAT, *Compt. rend.,* **156,** 424 (1913).
[86] SABATIER and MURAT, *Compt. rend.,* **156,** 751 (1913).
[87] WILLSTÄTTER and KAMETAKA, *Berichte,* **41,** 1480 (1908).
[88] ROZANOV, *J. Russian Phys. Chem. Soc.,* **48,** 168 (1916), *C. A.,* **11,** 454.

Methyl-cyclopropene yields *isobutane* at 170–180°: [89]

$$CH \diagdown \\ \cdot \quad \diagup C.CH_3 \quad \rightarrow \quad CH_3 \diagdown \\ CH_2 \diagup \qquad CH_3 \diagup CH.CH_3.$$
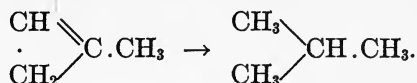
Dimethylmethylene-cyclo-propane gives *isohexane* at 160°: [90]

$$CH_2 \diagdown \\ \cdot \quad \diagup C : C(CH_3)_2 \quad \rightarrow \quad CH_3.CH_2CH_2CH(CH_3)_2 \\ CH_2 \diagup$$
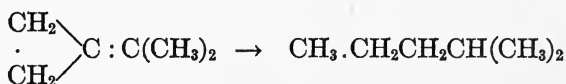
473. Tetramethylene Ring. *Cyclobutane* furnishes *butane,* while *cyclobutene,* at 180°, passes first into *cyclobutane* and then into *butane.*[91]

474. Pentamethylene Ring. *Cyclopentadiene* is regularly hydrogenated to *cyclopentane.*[92]

475. Hexamethylene Ring. *Cyclohexene,* C_6H_{10}, is readily reduced to the *cyclohexane* condition by nickel below 180°. The same is true of the *cyclohexadienes.*

All the *cyclohexene* hydrocarbons are readily hydrogenated by nickel to the *cyclohexane* hydrocarbons. Thus the ethylene hydrocarbons formed from the three *dimethyl-cyclohexanols* readily furnish the three dimethyl-cyclohexanes.[93] *Methyl-ethyl-1,2-cyclohexene* regularly passes into the corresponding saturated derivative.[94]

Menthene, $CH_3 . C_6H_8 . C_3H_7$, submits to regular hydrogenation at 175° to give *p.methyl-isopropyl-cyclohexane,* or *menthane,* identical with that formed from cymene and accompanied by certain amounts of the same secondary products [95] (448).

Phenyl-cyclohexene(1,1) is readily changed to *phenyl-cyclohexane* by a slightly active nickel. The same is true of *cyclohexyl-cyclohexene*(1,1), which furnishes *dicyclohexyl.*[96]

476. Acetyl-cyclohexane, $CH_6 . CO . C_6H_{11}$, is hydrogenated by nickel at 160°, without affecting the ketone group, to give *hexahydroacetophenone.*[97]

Ethyl tetrahydrobenzoate, $C_6H_9 . CO_2C_2H_5$, is transformed into

[89] Mereshkowski, *J. Russian Phys. Chem. Soc.,* **46**, 97 (1914), *C. A.,* **8**, 1965.
[90] Zelinsky, *Berichte,* **40**, 4743 (1907).
[91] Willstätter and Bruce, *Berichte,* **40**, 4456 (1907).
[92] Eijkman, *Chem. Weekblad,* **1**, 7 (1903).
[93] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **10**, 552, 555 and 559 (1907).
[94] Murat, *Bull. Soc. Chim.* (4), **1**, 774 (1907).
[95] Sabatier and Senderens, *Compt. rend.,* **132**, 1256 (1901).
[96] Sabatier and Murat, *Compt. rend.,* **154**, 1390 (1912).
[97] Darzens and Rost, *Compt. rend.,* **151**, 758 (1910).

ethyl hexahydrobenzoate, and the ester of *cyclohexene-acetic* acid, $C_6H_9 . CH_2 . CO_2H$, into that of *hexahydrophenyl-acetic* acid.[98]

Carvone adds hydrogen to its double bond and its ketone group passes into the alcohol, forming a mixture of *hydrocarvols.*[99]

477. Terpenes. The terpenes with *two double bonds* add $2H_2$ with nickel at 180°, while the terpenes with *one double bond* usually add only H_2.

Limonene gives *menthane,* identical with that from *menthene* and *cymene* with the same secondary products. The same is true of *sylvestrene* and *terpinene.*

Pinene is readily transformed at 170–180° into *dihydropinene,* $C_{10}H_{18}$, boiling at 166°, identical with that prepared by the action of hydroiodic acid (Berthelot).

The *camphene* (from an unknown source), melting at 41°, studied by Sabatier and Senderens, added H_2 with difficulty at 165–175° to furnish a *camphane,* $C_{10}H_{18}$, boiling at 164° and appearing to be identical with that which Berthelot had previously isolated.[100]

The camphene from pinene hydrochloride gave a mixture of a solid *camphane,* melting at 65–67°, and liquid *camphane,* boiling at 160°.[101]

An inactive camphene melting at 47–49° was transformed into a solid *camphane,* melting at 60°, by a single hydrogenation over nickel.[102]

478. *Terpineol,* hydrogenated over nickel, even at a low temperature, around 125°, is changed to *hexahydrocymene.*[103]

α-*Thujene,* $CH_3 . C \overset{\displaystyle CH . CH_2}{\underset{\displaystyle CH . CH_2}{\diagdown \diagup}} C . CH(CH_3)_2$, changes into *hexahydrocymene.*[104]

479. Heptamethylene Ring. *Cycloheptadiene,* C_7H_{10}, hydrogenated over nickel at 180°, yields only *cycloheptane,* stable even with prolonged hydrogenation at 200°, but at 235° it seems to isomerize into *methyl-cyclohexane.*[105]

480. Octamethylene Ring. *Cyclo-octadiene,* C_8H_{12}, hydroge-

[98] DARZENS, *Compt. rend.,* **144**, 328 (1907).

[99] HALLER and MARTINE, *Compt. rend.,* **140**, 1302 (1905).

[100] SABATIER and SENDERENS, *Compt. rend.,* **132**, 1256 (1901).

[101] LIPP, *Annalen,* **382**, 265 (1911).

[102] NAMETKIN and MISS ABAUMOVSKAYA, *J. Russian Phys. Chem. Soc.,* **47**, 414 (1915), *C. A.,* **10**, 45.

[103] HALLER and MARTINE, *Compt. rend.,* **140**, 1393 (1905).

[104] ZELINSKY, *J. Russian Phys. Chem. Soc.,* **36**, 768 (1904).

[105] WILLSTÄTTER and KAMEKATA, *Berichte,* **41**, 1480 (1908).

nated very slowly over nickel at 180°, gives *cyclo-octane*, C_8H_{16},[106] which further hydrogenation at 200–250° appears simply to isomerize into *dimethyl-cyclohexane*.[107]

Bicyclo-octene, at 150°, furnishes *bicyclo-octane*, boiling at 140°.[108]

481. Naphthalene Nucleus. *Naphthalene* is transformed at 200° by nickel into *tetrahydronaphthalene*,[109] boiling at 205°,[110] while at 175°, *decahydronaphthalene*, or *naphthane*, boiling at 187°, is formed.[111]

α-Naphthol, by means of two successive hydrogenations at 170° and 135°, respectively, is transformed into decahydro-α-naphthol, melting at 62°.

Likewise by hydrogenation at 170° and then at 150°, β-naphthol yields decahydro-β-naphthol, melting at 75°.[112]

482. *Acenaphthene*, $C_{10}H_6$$\begin{matrix} \diagup CH \\ | \quad _2, \\ \diagdown CH_2 \end{matrix}$ which is related to naphthalene in constitution, is transformed by nickel at 210°, as well as at 250°, into the *tetrahydro–*, $C_{12}H_{14}$, boiling at 254°.[113]

483. Anthracene Nucleus. *Anthracene* is hydrogenated in steps, more hydrogen being taken up at lower temperatures. At 260° *tetrahydroanthracene*, $C_{14}H_{14}$, melting at 89°, is formed, while at 200°, *octohydroanthracene*, melting at 71°, is obtained. By using a very active recently prepared nickel, it is possible to transform the *octohydro–* into *perhydroanthracene*, $C_{14}H_{24}$, melting at 88°.[114]

484. Phenanthrene Nucleus. *Phenanthrene*, $C_{14}H_{10}$, hydrogenated at 160° over a very active nickel, gave a mixture of the *hexa-*

[106] WILLSTÄTTER and VERAGUTH, *Berichte*, **40**, 957 (1907).

[107] WILLSTÄTTER and WASER, *Berichte*, **44**, 3444 (1911).

[108] WILLSTÄTTER and VERAGUTH, *Berichte*, **41**, 1480 (1908).

[109] The tetrahydro has d. 0.915^{20} and boils at 205–207° and is known as tetralin while the dekahydro is known as dekalin and has d. 0.8827^{20} and boils at 189–191°. Tetralin spirits is a mixture of the two. These are coming to be important as turpentine substitutes, particularly in Europe. See DE KEGHEL, *Rev. chim. ind.*, **29**, 173–178 (1920), *C. A.*, **14**, 3803; also SHROETER, *Annalen*, **426**, 1 (1922).— E. E. R.

[110] SABATIER and SENDERENS, *Compt. rend.*, **132**, 1257 (1901).

[111] LEROUX, *Compt. rend.*, **139**, 672 (1904).

[112] LEROUX, *Compt. rend.*, **141**, 953 (1905). *Ann. Chim. Phys.* (8), **21**, 483 (1910).

[113] SABATIER and SENDERENS, *Compt. rend.*, **132**, 1257 (1901). GODCHOT, *Bull. Soc. Chim.* (4), **3**, 529 (1908).

[114] GODCHOT, *Ann. Chim. Phys.* (8), **12**, 468 (1907).

hydro–, boiling at 305°, and the *octohydro–,* $C_{14}H_{18}$, boiling at 280°.[115] These results are different from those obtained by Schmidt and Metzger, who got only *dihydrophenanthrene* at 150°,[116] and from those of Padoa and Fabris, who obtained a mixture of the solid *dihydro–* and the liquid *tetrahydro–* at 200°, but were able to get the *dodecahydro–* at 175°.[117]

485. Complex Rings. *Pyrrol,* when hydrogenated over nickel at 180–190°, gives 25% of *pyrrolidine,* C_4H_9N, with a small quantity of a substance which appears to be *hexahydro-indoline.*[118]

486. *Pyridine* is only slowly attacked by hydrogenation over nickel between 120 and 220°, and does not yield any *piperidine;* there is opening of the ring with the formation of some *amyl-amine.*[119]

487. *Furfuryl-ethyl-carbinol* yields *tetrahydrofurfuryl-ethyl-carbinol* on hydrogenation at 175°.[120]

Methyl-α-fufurane adds $2H_2$ at 190° to give *tetrahydro-methyl-*

$$\alpha\text{-}furfurane, \quad \begin{array}{c} CH_2.CH_2 \\ | \qquad\qquad \rangle O \\ CH_2.CH{-\!-\!-}CH_3 \end{array} \quad .$$

If the hydrogenation is pushed, the ring is opened and *methyl-propyl-ketone* is formed, finally *methyl-propyl-carbinol,* or *pentanol*(2).[121]

488. *Quinoline,* when hydrogenated over a very active nickel at 160–190°, adds $2H_2$ to the pyridine ring to form *tetrahydroquinoline* in excellent yield.

Likewise 6–*methyl-quinoline* is readily hydrogenated to the corresponding *methyl-tetrahydroquinoline.*[122]

By carrying out the hydrogenation at 130–140°, over a very active nickel, *decahydroquinoline* may be obtained. Likewise *quinaldine* furnishes *decahydroquinaldine* in excellent yield.[123]

489. By hydrogenating quinoline at a higher temperature, the normal addition of hydrogen does not take place, but the ring is opened to yield *ethyl-o.toluidine,* which does not remain as such but closes the ring, with loss of hydrogen to give α-methyl-indol:[124]

[115] BRETEAU, *Compt. rend.,* **140**, 942 (1905).
[116] SCHMIDT and METZGER, *Berichte,* **40**, 4240 (1907).
[117] PADOA and FABRIS, *Gaz. Chim. Ital.,* **39** (1), 333 (1909).
[118] PADOA, *Gaz. Chim. Ital.,* **36** (2), 317 (1906)..
[119] SABATIER and MAILHE, *Compt. rend.,* **144**, 784 (1907).
[120] DOURIS, *Compt. rend.,* **157**, 722 (1913).
[121] PADOA and PONTI, *Lincei,* **15** (2), 610 (1906), *C.,* **1907** (1), 570.
[122] DARZENS, *Compt. rend.,* **149**, 1001 (1909).
[123] SABATIER and MURAT, *Compt. rend.,* **158**, 309 (1914).
[124] PADOA and CARUGHI, *Lincei,* **15**, 113 (1906), *C.,* **1906** (2), 1011.

```
  CH    CH          CH                      CH
 /   \  /          /   \  /                /   \
HC    C    CH   HC    C.CH₃         →    HC    C——CH
 |    |    |  →  |     |                  |    |      ‖
HC    C    CH   HC    C.NH.CH₂          HC    C    C.CH₃
 \   /  \       \   /                    \   /  \  /
  CH    N        CH      CH₃              CH    NH
```

490. *Carbazol, diphenyl-imide,* when hydrogenated over nickel at 200° under 10 atmospheres pressure, gives $\alpha\beta$-dimethyl-indol: [125]

```
   ╱CH╲         ╱CH╲              ╱CH╲
 HC    C————C    CH       HC    C————C.CH₃
  |    |    |    |    →     |    |    |
 HC    C    C    CH→      HC    C    C.CH₃
   ╲CH╱  ╲N╱  ╲CH╱          ╲CH╱  ╲NH╱
```

491. *Acridine* is slowly hydrogenated over nickel at 250–270° to $\alpha\beta$-*dimethyl-quinoline:* [126]

```
   ╱CH╲   ╱N╲   ╱CH╲                ╱CH╲   ╱N╲
 HC    C    C    CH        HC    C    C.CH₃
  |    |    |    |    →      |    ‖    |
 HC    C    C    CH        HC    C    C.CH₃
   ╲CH╱ ╲CH╱ ╲CH╱            ╲CH╱ ╲CH╱
```

9.   Carbon Disulphide

492. When carbon disulphide vapors are carried by an excess of hydrogen over nickel at 180°, a volatile, extremely ill-smelling substance is produced which gives a yellow mercury salt, a white cadmium salt, and brown lead and copper salts, and which appears to be *methylene-dithiol,* $H_2C(SH)_2$. [127]

Hydrogenations with Decompositions

493. Catalytic nickel quite frequently exercises a more or less intense decomposing action on the molecules: in such cases not only the original compound but also the fragments resulting from its decomposition are hydrogenated.

Hydrocarbons. We shall study in Chapter XXI the decompositions that hydrocarbons undergo at high temperatures in the presence of nickel and other catalysts. The study of the simultaneous hydrogenations can not be separated from that of the decompositions and molecular condensations resulting therefrom.

[125] Padoa and Chiaves, *Lincei,* 16 (2), 762 (1907), *C.,* 1908 (1), 649.
[126] Padoa and Fabris, *Lincei,* 16 (1), 921 (1907), *C.,* 1907 (2), 612.
[127] Sabatier and Espil, *Bull. Soc. Chim.* (4), 15, 228 (1914).

494. Aliphatic and Aromatic Ethers. *Aliphatic* ethers resist hydrogenation over nickel quite well, but when it is carried out above 250°, there is decomposition into hydrocarbon and alcohol which is then attacked, furnishing the products of the hydrogenation of its debris.

Thus *ethyl ether* gives ethane and alcohol which gives the fragments of acetaldehyde, of which the carbon monoxide is partly changed to methane: [128]

$$(C_2H_5)_2O + H_2 = C_2H_6 + CH_3 . CH_2OH$$
then
$$CH_3 . CH_2OH = CH_4 + CO + H_2$$
$$CO + 3H_2 = CH_4 + H_2O.$$

Aromatic ethers undergo an analogous decomposition with nickel, this taking place at moderate temperatures with the mixed *alkyl phenyl ethers* and greatly diminishing the yields of the mixed *alkyl-cyclo-aliphatic ethers* which are made by their hydrogenation.

In the hydrogenation of *anisol* to *methoxy-cyclohexane* (464), there is the production of certain amounts of *methyl alcohol* and *cyclohexane*.[128] If the operation is carried on above 300°, there is no hydrogenation of the nucleus and scission is rapid in the same manner as with *aliphatic ethers*.

We have two reactions:

$$C_6H_5 . O . R + H_2 = RH + \underset{\text{phenol}}{\underline{C_6H_5 . OH}}$$
and
$$C_6H_5 . O . R + H_2 = C_6H_6 + \underset{\text{alcohol}}{\underline{R . OH}}$$

the alcohol itself being more or less broken down by the hydrogenation.

This is the case with the *methyl* ethers of *phenol,* of the three *cresols,* of *α-naphthol,* etc., and also with *phenyl oxide* which is the most resistant to decomposition.[129]

495. Phenyl Isocyanate. Phenyl isocyanate, when hydrogenated over nickel at 190°, breaks up into two portions which are hydrogenated separately:

$$C_6H_5 . N : CO = CO + C_6H_5 . N-.$$

We obtain *aniline* and *carbon monoxide* which yields *methane* with the formation of water. This reacts quantitatively with the original compound to give *carbon dioxide* and solid *diphenyl-urea*.[130]

[128] SABATIER and SENDERENS, *Bull. Soc. Chim.* (3), **33**, 616 (1905).

[129] MAILHE and MURAT, *Bull. Soc. Chim.* (4), **11**, 122 (1912).

[130] SABATIER and MAILHE, *Compt. rend.,* **144**, 825 (1907).

496. Amines. Various amines hydrogenated over nickel at above 300–350°, tend to form *ammonia* and a hydrocarbon. This reaction which takes place readily with aliphatic amines has already been mentioned with *aniline* (378). It takes place with the homologs of aniline, with *benzyl-amine* and with the *naphthyl-amines*.

Hexamethylene-tetramine is completely decomposed yielding ammonia, *trimethyl-amine* and *methane:* [131]

$$N(CH_2 . N : CH_2)_3 + 9H_2 = N(CH_3)_3 + 3NH_3 + 3CH_4.$$

497. Compounds Containing –N . N–. *Phenylhydrazine*, hydrogenated above 210°, is split into *ammonia* and *aniline*, accompanied by *cyclohexyl-amine*, *dicyclohexyl-amine*, and even by *benzene* and *cyclohexane*.[132]

The main reaction is:

$$C_6H_5 . NH . NH_2 + H_2 = NH_3 + C_6H_5 . NH_2.$$

Azobenzene, $C_6H_5 . N : N . C_6H_5$, hydrogenated at 290°, yields *aniline* chiefly.[132]

Indol. On hydrogenation over nickel at 200°, *indol* is split into *o.toluidine* and *methane:* [133]

$$C_6H_4 \underset{\displaystyle \diagdown NH \diagup}{\overset{\displaystyle \diagup CH \diagdown}{}} CH + 3H_2 = C_6H_4 \underset{\displaystyle \diagdown NH_2}{\overset{\displaystyle \diagup CH_3}{}} + CH_4$$

[131] Grassi, *Gaz. Chim. Ital.*, **36** (2), 505 (1906).
[132] Sabatier and Senderens, *Bull. Soc. Chim.* (3), **35**, 259 (1906).
[133] Carrasco and Padoa, *Lincei*, **14** (2), 699 (1906), *C.*, **1906** (2), 683.

CHAPTER X

HYDROGENATIONS (Continued)

HYDROGENATIONS IN GASEOUS SYSTEM (Continued)

I. — USE OF VARIOUS CATALYSTS

498. Nickel as a hydrogenation catalyst can be replaced by various finely divided metals, such as cobalt, iron, copper, platinum, and the platinum metals, particularly palladium.

Cobalt

499. Finely divided cobalt such as is produced by the reduction of the oxide in the hydrogenation tube itself, seems to be able to take the place of nickel in all the various reactions which nickel can catalyze.

But its use is disadvantageous because its activity is less and more easily destroyed than that of nickel; because higher temperatures are required when using it; and also because the reduction of its oxide is practicable only in the neighborhood of 400°, and hence the oxide resulting from spontaneous oxidation during the time the apparatus is cold and out of use, can not be reduced at temperatures below 250° such as are commonly used in hydrogenations.

500. **Ethylene Hydrocarbons.** When a mixture of *ethylene* and an excess of hydrogen is passed over cold reduced cobalt, immediate action takes place with the production of *ethane,* and the end of the cobalt layer becomes hot. The heated portion moves slowly along the metal and the evolution of heat finally ceases and the production of ethane stops also, doubtless because the cobalt is slightly carbonized in the course of the reaction and its activity so diminished that it is unable to continue the reaction without the aid of external heat.

At 150°, the hydrogenation of ethylene continues indefinitely, but the cobalt is slowly weakened, more rapidly than nickel.

Above 300°, the disturbance due to the action of the cobalt on the ethylene (910) appears and the issuing gases contain methane and carry along small amounts of liquid hydrocarbons.[1]

[1] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 344 (1905).

The action of cobalt on the homologs of ethylene is similar to that of nickel but weaker.

501. Acetylene.   Reduced cobalt, entirely free from nickel, can serve to hydrogenate acetylene, but there is no reaction in the cold. The fixation of hydrogen begins at about 180°, and the ethane produced is accompanied by a small amount of liquid hydrocarbons, which are more abundant if the reaction is carried on at 250°.[2]

502. Benzene and its Homologs.   Reduced cobalt can effect the direct hydrogenation of benzene and its homologs at 180°, but its activity falls off rather rapidly.[3]

503. Aliphatic Aldehydes and Ketones.   Cobalt can transform aliphatic aldehydes and ketones into the alcohols below 180°, but is less active than nickel.   Under identical conditions, with the same apparatus, the same temperature, the same velocity of hydrogen, and the same rate of admission of *acetone,* the yield of *isopropyl alcohol* was about 83% with nickel as catalyst but slightly less than 50% with cobalt.[4]

504. Carbon Monoxide and Dioxide.   Reduced cobalt can cause the transformation of *carbon monoxide* into *methane,* as does nickel, but the reaction does not begin till about 270°.   It is rapid at 300°, but is opposed more strongly, than is the case with nickel, by the decomposition of carbon monoxide into carbon and the dioxide (615). This decomposition is as rapid with cobalt as with nickel, while the hydrogenation is slower with the cobalt.

The hydrogenation of carbon dioxide is effected by cobalt from 300° up.   It is rapid at 360° and even more so at 400° and is accomplished without any complications.[5]

Iron

505. Finely divided iron, obtained by the reduction of its oxides, can be substituted for nickel as a hydrogenation catalyst in certain cases, but is less active than nickel and even less active than cobalt. Besides, it has the marked disadvantage of being much more difficult to prepare from its oxide.   Between 400 and 500° it is necessary to continue the action of hydrogen from six to seven hours to obtain complete reduction.   When the metal is reduced more rapidly at higher temperatures, it is no longer pyrophoric and has only slight activity.

[2] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 352 (1905).
[3] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 368 (1905).
[4] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 400 and 403 (1905).
[5] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 424 (1905).

506. Ethylene Hydrocarbons. Iron causes the hydrogenation of ethylene only above 180°, and its activity decreases with the slow carbonizing of the metal.

Acetylene. The hydrogenation of *acetylene* does not commence till above 180°, and always gives rise to the formation of rather large amounts of colored hydrocarbons, containing higher ethylene hydrocarbons soluble in sulphuric acid, aromatic hydrocarbons, and only a small amount of saturated hydrocarbons. The odor and appearance of the product suggest certain *natural petroleums of Canada.*

To a certain extent, iron can cause the hydrogenation of *aldehydes,* *ketones* and *nitro compounds,* but is incapable of transforming carbon monoxide and dioxide into *methane* or of adding hydrogen to the *benzene nucleus.*[6]

Copper

507. Reduced copper is a useful catalyst for certain hydrogenations. For such its use is advantageous on account of its ease of preparation, the low temperature, below 180°, at which its oxide can be reduced, and its resistance to poisons which is more marked than with other metal catalysts.

508. Reduction of Carbon Dioxide. Copper, even in its most active form (59), is incapable of causing the direct hydrogenation of *carbon monoxide* to *methane* and does not show any action on mixtures of carbon monoxide and hydrogen below 450°.

It is the same way with mixtures of hydrogen and *carbon dioxide* below 300°, but between 350 and 400° a special reaction appears gradually and is quite definite at 420–450°. There is reduction of the carbon dioxide into carbon monoxide and water, according to the equation:

$$CO_2 + H_2 = CO + H_2O.$$

Thus with a mixture of one part carbon dioxide to about three parts of hydrogen, a gas was obtained containing:

Carbon monoxide .... 10.0% by volume
Carbon dioxide .... 17.2% " "
Hydrogen .... 72.8% " "

More than a third of the carbon dioxide had been reduced to the monoxide. The proportion reduced is less when the concentration of hydrogen in the mixture is less.

[6] SABATIER and SENDERENS. *Ann. Chim. Phys.* (8), **4,** 345, 353, 368, 425, and 428 (1905).

In no case is even a trace of methane formed.[7]

509. Nitro Compounds.   *Copper* gives results analogous to those with nickel (373 to 378) only at higher temperatures.

Nitrous oxide is reduced to nitrogen at 180° and *nitric oxide* is changed into ammonia at the same temperature. Nitrogen peroxide gives *copper nitride* in the cold,[8] and it is only towards 180° that ammonia is produced. If the proportion of nitrogen peroxide becomes too great, there is incandescence followed by an explosion.[9]

510. *Nitromethane,* hydrogenated between 300 and 400°, gives, along with methyl-amine, a liquid of a more or less brown color with a disgusting odor in which appear crystals which are the methyl-amine·salt of nitromethane.

Between 300 and 400°, *nitro-ethane* gives *ethyl-amine* without notable complications.[10]

511. *Copper* is the best of all the finely divided metals for transforming aromatic nitro derivatives into the amines, since its very regular hydrogenating action affects only the –NO$_2$ group and does *not touch the aromatic nucleus. Nitrobenzene* is thus changed to *aniline* from 230° up, the reaction being rapid and very regular between 300 and 400°, and so long as the hydrogen is in excess, aniline is obtained in 98% yield containing only traces of nitrobenzene and the red azobenzene. The same metal can be used for a long time. The hydrogen can, without inconvenience, be replaced by *water gas,* the carbon monoxide of which acts usefully as a reducing agent to some extent since a part of it is transformed into carbon dioxide. The manufacture carried out with copper, a metal which is not costly and which serves for a long time and is easily regenerated without loss, and by means of a very cheap gas, can be carried on continuously and is very economical.[11]

Coppered pumice at 200–210° has been proposed as a substitute for copper.[12]

512. The manufacture of the *toluidines* from the *nitrotoluenes* is also advantageously carried on by copper at 300–400°, and likewise

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[7] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4,** 426 (1905).

[8] Sabatier and Senderens, *Ann. Chim. Phys.* (7), **7,** 401 (1896).

[9] Sabatier and Senderens, *Compt. rend.,* **135,** 278 (1902).

[10] Sabatier and Senderens, *Compt. rend.,* **135,** 227 (1902).

[11] Sabatier and Senderens, *Compt. rend.,* **133,** 321 (1901). — Sabatier, Vth. *Cong. Pure and Appl. Chem., Berlin,* 1903, II, 617. — Senderens, *French Patent,* 312,615 (1901).

[12] Badische, *English patent,* 6,409 of 1915. — *J. Soc. Chem. Ind.,* **35,** 920 (1916).

α-naphthyl-amine is readily obtained from *α-nitronaphthalene* at 330–350°.[13]

The *chlornitrobenzenes* are regularly transformed by copper into the *chloranilines* at 360–380°. On the contrary, copper gives poor results with the *dinitrobenzenes* and the *bromnitrobenzenes*.[14]

At 265° the results are excellent with the *nitrophenols* and the *nitranilines*.[15]

513. Esters of Nitrous Acid. *Nitrous esters* are regularly hydrogenated into the *amines*, over copper as well as over nickel, but at a higher temperature, 330–350°, the results are satisfactory for nitrites with heavy hydrocarbon chains, but are less so for *methyl nitrite* which gives brown products analogous to those obtained from nitromethane.[16]

514. Oximes. *Copper* accomplishes the regular hydrogenation of *aliphatic aldoximes* and *ketoximes* between 200 and 300° into primary and secondary amines without complications,[17] and the same may be said about *aliphatic amides*.[18]

515. Ethylene Compounds. Most often *copper* serves to add hydrogen to the ethylene double bond.

Ethylene, propylene and *α-octene* are changed to the corresponding saturated compounds at above 180°. However, *trimethylethylene* and *β-hexene* are not hydrogenated by copper, and it has been concluded that copper does not cause the hydrogenation of any except *α-ethylene* compounds, that is to say, those in which one of the CH_2 groups of the ethylene is not substituted.[19]

This limitation is not general since the vapors of *oleïc acid* are readily hydrogenated into *stearic acid* at around 300°. Water gas can be substituted for the pure hydrogen in this preparation and it has industrial possibilities.[20]

It may be noted that copper does not cause the hydrogenation of symmetrical *diphenyl-ethylene*, or *stilbene*, $C_6H_5 . CH : CH . C_6H_5$, of *cyclohexene*, C_6H_{10}, or of the *methyl-cyclohexenes*.[21]

516. The use of copper, which acts on the ethylene double bond

[13] SABATIER and SENDERENS, *Compt. rend.*, **135**, 225 (1902).

[14] MIGNONAC, *Bull. Soc. Chim.*, (4), **7**, 154, 270 and 504 (1910).

[15] BROWN and CARRICK, *J. Amer. Chem. Soc.*, **41**, 436 (1919).

[16] GAUDION, *Ann. Chim. Phys.* (8), **25**, 136 (1912).

[17] MAILHE, *Compt. rend.*, **140**, 1691 (1905) and **141**, 113 (1905).

[18] MAILHE, *Bull. Soc. Chim.* (3), **35**, 614 (1906).

[19] SABATIER and SENDERENS, *Compt. rend.*, **134**, 1127 (1902).

[20] SABATIER, *French patent*, 394,957 (1907).

[21] SABATIER, *50th. Cong. des Soc. Sav.* (1912). *Journ. Offic.*, 3628: April 11, 1912.

without attacking the aromatic nucleus, permits us to effect certain hydrogenations distinct from those obtained with nickel. *Phenyl-ethylene*, or *styrene*, $C_6H_5 . CH : CH_2$, which nickel changes into *ethyl-cyclohexane*, is transformed quantitatively at 180° by copper into *ethyl-benzene*.[22]

517. *Limonene*, $CH_3 . C_6H_8 . C \overset{\diagup CH_2}{\diagdown CH_3}$ which   nickel   readily

changes into menthane (477), gives only *dihydrolimonene*, $C_{10}H_{18}$, isomeric with *menthene*.[22]

518. **Acetylene Hydrocarbons.** Copper can not hydrogenate *acetylene* in the cold, the reaction being around 130° over copper with a light purple color and around 180° over copper of a clear red. Carried on with excess of hydrogen, the reaction always gives a certain proportion of liquid hydrocarbons along with the *ethane*.

When the amount of acetylene equals or surpasses the amount of hydrogen, the special condensing action of copper on acetylene (914) becomes evident: the copper swells up gradually on account of the formation of solid *cuprene*, $(C_7H_6)_x$ the gases evolved contain higher ethylene hydrocarbons and a mixture of liquid ethylene and aromatic hydrocarbons (benzene, and homologs and styrene) is collected.

A gas mixture containing 21 H_2 to 19 C_2H_2 gave, at 150° over violet copper, a condensation of materials containing 25 C with about 65% carbon, one third as cuprene and the other two thirds as liquid hydrocarbons.[23]

519. The hydrogenation of *α-heptine* over copper at below 200°, gave a little *heptane*, but chiefly *heptene, diheptene*, and *triheptene*.[24]

520. *Phenyl acetylene*, $C_6H_5 . C : CH$, which nickel transforms easily into ethyl-cyclohexane (451), gave by hydrogenation over copper between 190 and 250°, *ethyl-benzene*, $C_6H_5 . CH_2 . CH_3$, accompanied by a little *phenyl-ethylene* and a nearly equal amount of symmetrical *diphenyl-butane*, $C_6H_5 . CH_2 . CH_2 . CH_2 . CH_2 . C_6H_5$, a well crystallized solid.[25]

521. **Nitriles.** *Copper* can transform *nitriles* into primary and secondary amines [26] in the same manner that nickel does. It acts

[22] SABATIER and SENDERENS, *Compt. rend.*, **132,** 1255 (1901).

[23] SABATIER and SENDERENS, *Compt. rend.*, **130,** 1559 (1900).

[24] SABATIER and SENDERENS, *Compt. rend.*, **135,** 87 (1902).

[25] SABATIER and SENDERENS, *Compt. rend.*, **135,** 88 (1902).

[26] SABATIER and SENDERENS, *Compt. rend.*, **140,** 482 (1905) and *Bull. Soc. Chim.* (3), **33,** 371 (1905).

similarly on the *carbyl-amines*,[27] but its action is less rapid than that of nickel.

522. Aliphatic Aldehydes and Ketones. Below 200°, copper can transform these slowly into the alcohols, but the inverse action usually preponderates and this makes the use of copper less advantageous.

Furthermore, copper is incapable of transforming the oxides of carbon into *methane* or of hydrogenating the *aromatic nucleus*.

523. Aromatic Ketones. When *benzophenone* is hydrogenated at 350° over copper with a violet tint, prepared by the reduction of the hydroxide (59), *diphenyl-methane* is formed directly.[28]

Platinum

524. *Platinum black* can be used for direct hydrogenation in quite a large number of cases and its activity is greater than that of copper though less than that of nickel. Its activity is greater, the more tenuous the black and the more recently it has been prepared. It is rapidly exhausted and this fact taken together with the high cost of the metal renders its use generally less advantageous.

Platinum *moss,* or *sponge,* behaves the same way but with less activity, which is usually not manifested except at a higher temperature.

525. Union of Carbon and Hydrogen. The presence of finely divided platinum on the carbon accelerates its direct combination with hydrogen to form *methane* at 1200°, the limit of the combination, 0.53%, not being altered.[29]

526. Ethylene Compounds. A mixture of *ethylene* and hydrogen is transformed into *ethane* in the cold in the presence of platinum black.[30] But after some time the slight carbonization of the metal prevents the reaction from proceeding at the ordinary temperature and it is necessary to heat to 120°, or even to 180°, to obtain a rapid formation of ethane.[31]

Analogous results are obtained with *propylene.*

The vapors of *amyl oleate* can be hydrogenated over platinized asbestos to *amyl stearate.*[32]

527. Acetylene Hydrocarbons. *Acetylene* combines with hydro-

[27] SABATIER and MAILHE, *Ann. Chim. Phys.*, (8) **16**, 95 (1909).

[28] SABATIER and MURAT, *Compt. rend.*, **158**, 761 (1914).

[29] PRING, *J. Chem. Soc.*, **97**, 498 (1910).

[30] VON WILDE, *Berichte*, **7**, 352 (1874).

[31] SABATIER and SENDERENS, *Compt. rend.*, **131**, 40 (1900).

[32] FOKIN, *J. Russian Phys. Chem. Soc.*, **38**, 419 (1906), *C.*, **1906** (2), 758.

gen in the cold in the presence of platinum black, giving first ethylene and then ethane.[30]

In presence of an excess of hydrogen, acetylene is entirely transformed into pure ethane without any side reactions.

At 180° the same reaction takes place more rapidly but there is the formation of a certain amount of higher liquid hydrocarbons. By augmenting the proportion of acetylene in the mixture, *ethylene* becomes the main product but some ethane is always formed even though unchanged acetylene remains.

If the proportion of acetylene becomes great enough, with the *platinum black* at 180°, a certain amount of smoky decomposition of the gas is observed and this ends with incandescence, as is the case with nickel (914).

Platinum sponge is not active in the cold and does not effect the hydrogenation of acetylene except above 180°.[33]

528. Hydrocyanic Acid. Platinum black can hydrogenate hydrocyanic acid to *methyl-amine* at 116°, but the cyanidation of the metal soon diminishes its activity and stops the reaction.[34]

529. Nitro Compounds. Nitrogen oxides, either *nitric oxide* or the *dioxide*, are readily reduced to *ammonia* with the aid of platinum sponge which is thereby heated to incandescence.[35]

530. *Nitromethane* is hydrogenated over platinum sponge at 300°, more slowly than over copper but with analogous results (510).[36]

531. Various forms of platinum, black, sponge, and platinized asbestos, can cause the transformation of *nitrobenzene* into aniline, but their catalytic power is low and, if the hydrogen is not in large excess, there is incomplete reduction with the formation of crystallized hydrazobenzene.[37]

532. Aliphatic Aldehydes and Ketones. Finely divided platinum is unsuitable for the regular transformation of these into the alcohols, since at the temperatures which must be used, which are above 200°, the metal acts powerfully to break up the aldehyde molecule into carbon monoxide and hydrocarbon (622).

533. Finely divided platinum, even in the form of highly active black, has proved powerless to effect the direct hydrogenation of *carbon monoxide* or *dioxide* to methane. There is no action even up to 450°.[38]

[33] Sabatier and Senderens, *Compt. rend.*, **131**, 40 (1900).
[34] Debus, *J. Chem. Soc.*, **16**, 249 (1863).
[35] Kuhlmann, *Compt. rend.*, **7**, 1107 (1838).
[36] Sabatier and Senderens, *Compt. rend.*, **135**, 226 (1902).
[37] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4**, 414 (1905).
[38] Sabatier and Senderens, *Compt. rend.*, **134**, 514 and 689 (1902).

534. Aromatic Nucleus. Recently prepared *platinum black* can transform benzene into *cyclohexane* at 180° for a time, but its activity diminishes rapidly and soon disappears.

Platinum sponge has not this power.[39]

According to Zelinsky, platinum is as well able to hydrogenate *benzene, toluene,* the three *xylenes* and *ethyl-benzene,* as is nickel.[40]

He states the same about palladium.

535. Polymethylene Rings. *Spirocyclane,* with the aid of platinum, first adds H_2 to form ethyl trimethylene, which passes to pentane by a second addition: [41]

$$\underset{CH_2}{\overset{CH_2}{\diagdown}}C\underset{CH_2}{\overset{CH_2}{\diagup}} \cdot \rightarrow \cdot \underset{CH_2}{\overset{CH_2}{\diagdown}}CH.CH_2CH_3 \rightarrow CH_3.CH_2.CH_2.CH_2.CH_3.$$

Cyclo-octatetrene adds $4H_2$ with the aid of platinum sponge to form *cyclooctane.*[42]

Palladium

536. Palladium, previously charged with hydrogen, is able to effect varied hydrogenations, such as the transformation of nitrobenzene into aniline, nitromethane into methyl-amine, and nitrophenols into aminophenols (Graham). It is easy to foresee that it can serve equally well as a hydrogenation catalyst, the intermediate hydride which enables it to accomplish these results being notably stable in this case.

The formation of aniline by the action of hydrogen on nitrobenzene in the presence of palladium was shown by Saytzeff.[43]

Carbon monoxide can be reduced in the cold, or better, at 400°, to *methane* in the presence of palladium sponge.[44]

Phenanthrene, carried over palladium sponge at 150–160° by a current of hydrogen, gives a mixture of *tetrahydro-* and *octohydro-phenanthrene.*[45]

Unfortunately the excessive price of palladium restricts its useful applications.

[39] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 368 (1905).

[40] ZELINSKY, *J. Russian Phys. Chem. Soc.,* **44,** 274 (1912).

[41] ZELINSKY, *J. Russian Phys. Chem. Soc.,* **44,** 275 (1912).

[42] WILLSTÄTTER and WASER, *Berichte,* **44,** 3423 (1911).

[43] KOLBE and SAYTZEFF, *J. prakt. Chem.* (2), **4,** 418 (1871).

[44] BRETEAU, *Etude sur les meth. d'hydrogenation,* 1911, p. 22.

[45] BRETEAU, *Ibid.,* p. 24.

II. — HYDROGENATION BY NASCENT HYDROGEN

537. Certain catalyses yield hydrogen and the gas so produced can be immediately employed for hydrogenation purposes. We can thus use as sources of active hydrogen, *alcohol* vapors, *formic acid,* and even a mixture of *water* and *carbon monoxide.*

Hydrogenation by Alcohol Vapors

538. Primary and secondary alcohols can, under the influence of various catalysts, be decomposed into aldehydes and ketones and hydrogen (653): the hydrogen thus set free can act in the nascent state on substances the vapors of which are mixed with the alcohols.

Copper can easily realize such reactions, but we can attribute to its action the hydrogenation correlative to the decomposition.

We can use *mixed oxide catalysts* (675) and even *dehydrating* catalysts, such as thoria, the presence of the substance that can be hydrogenated orienting the decomposition of the alcohol in the direction of the separation of hydrogen and greatly diminishing the extent of the dehydration reaction.

Thus over *thoria* at 420°, *benzhydrol,* with *ethyl alcohol* in excess, gives much *diphenyl-methane* accompanied by a little benzophenone and tetraphenyl-ethane (720): *acetaldehyde* is evolved and the gases arising from its decomposition.

The alcohol most suitable for this sort of hydrogenation is methyl alcohol on account of its great tendency to produce formaldehyde and particularly the products of its decomposition, carbon monoxide and hydrogen (693):

$$H \cdot CH_2OH = 2H_2 + CO.$$

The vapors of the substance to be hydrogenated are passed over thoria at 420°, with an excess of methyl alcohol, the hydrogenation is advantageously accomplished in all cases in which the product is stable at that temperature. Thus *benzophenone* and *benzhydrol* are changed almost completely into *diphenyl-methane,* while *benzyl alcohol* and *benzaldehyde* give *toluene, acetophenone* furnishes *ethyl-benzene,* and *nitrobenzene* yields *aniline.*[46][47]

[46] Sabatier and Murat, *Compt. rend.,* **157,** 1499 (1913). — *Bull. Soc. Chim.* (4), **15,** 227 (1914).

[47] By using 2.5 moles of ethyl alcohol to 1 of benzaldehyde, and passing the mixed vapors over ceria on asbestos at 300–300°, benzyl alcohol is obtained along with acetaldehyde. Similarly citronellol is formed from citronellal and phenylethyl alcohol from phenylacetaldehyde. The yields are variable and the catalyst is rapidly fouled, probably on account of the formation of condensation products of the aldehydes either alone or with each other. See article by Milligan and myself, *Jour. Amer. Chem. Soc.,* **44,** 202 (1922). — E. E. R.

Hydrogenation by the Vapors of Formic Acid

539. The vapors of *formic acid* passing over various catalysts, finely divided platinum, copper or nickel reduced from their oxides, cadmium, stannous oxide or zinc oxide, are decomposed below 300° into carbon dioxide and hydrogen (824):

$$HCO_2H = H_2 + CO_2.$$

This hydrogen can be used to hydrogenate substances the vapors of which are present in the system. Under these conditions, using nickel at 300°, *acetophenone* is changed to *ethyl-benzene, phenyl-ethyl-ketone* into *propyl-benzene,* and *benzophenone* into *diphenyl-methane.*

Thoria, alumina and zirconia effect the same hydrogenations above 300°, but the oxides of manganese appear to be inactive.[48]

Hydrogenation by the Mixture of Carbon Monoxide and Water

540. The mixture $CO + H_2O$ can be transformed into $CO_2 + H_2$, the reaction being favored by the temporary combination of the carbon dioxide with the catalyst or by the immediate utilization, thanks to the catalyst, of the hydrogen to hydrogenate the carbon monoxide into methane. The reaction then becomes:

$$4CO + 2H_2O = 3CO_2 + CH_4.$$

It is found, in fact, that a mixture of steam and carbon monoxide passing over *lime* at above 1000° gives the above reaction and we have the following reaction at the same time:

$$CO + H_2O = CO_2 + H_2.$$

As calcium carbonate is entirely decomposed at this temperature, the lime acts as a true catalyst. By separating the carbon dioxide, we can obtain a mixture containing:

Hydrogen .... 88% by volume
Methane [49] 12%

The same mixture passing over *iron wool* likewise gives methane in varying amounts:

At   250° .... 7.3% by volume
At   950° 11.2%
At 1250° 7.1%

By the use of fine *nickel* turnings a maximum content of 12.5% of

[48] MAILHE and DE GODON, *Bull. Soc. Chim.* (4), 21, 61 (1917).
[49] VIGNON, *Compt., rend.,* 156, 1995 (1913).

methane is obtained at 400°. With *copper* turnings, almost no result is obtained at 500°, and the maximum, 6.3%, is obtained at 700°.

Precipitated *silica* gives a maximum of 8.4% at 700°, while for *alumina*, obtained by calcining the hydroxide, the maximum, 3.8%, is obtained at 950°, and for *magnesia*, a maximum of 6.7% at 900°.[50]

[50] VIGNON, *Compt. rend.*, **157,** 131 (1913). — *Bull. Soc. Chim.* (4), **13,** 889 (1913).

CHAPTER XI

HYDROGENATIONS (Continued)

DIRECT HYDROGENATIONS OF LIQUIDS IN CONTACT WITH METAL CATALYSTS

541. We have explained the phenomena of direct hydrogenation as accomplished by various finely divided metals when the substance to be hydrogenated is brought in contact with the metal in the gaseous form, by assuming a sort of *hydride* of the metal, an unstable compound formed rapidly and decomposed rapidly in the act of hydrogenating the substance (165). This explanation does not necessarily require that the substance to be hydrogenated be in the gaseous form as we can see that the same reaction can be accomplished with a liquid material intimately mixed with a finely divided metal capable of taking up hydrogen. In order that the hydrogen may come into contact with the metal it is necessary that its solubility in the liquid be made sufficiently great by using low temperatures at the ordinary pressure, or a high pressure of hydrogen if it is necessary to heat.

An energetic and continuous agitation, constantly renewing the contact of the catalyst with the unchanged portions of the liquid will be most useful.

Furthermore, in order for the metal to be able to preserve its activity, it must not be oxidisable at the working temperature, or this temperature must be high enough to assure the reduction by the hydrogen in the system of any oxide formed.

542. From these conditions may be derived several methods which give results in general identical with those obtained by the method of Sabatier and Senderens of hydrogenating vapors over nickel, and which may offer great advantages in some cases.

The first attempt to hydrogenate substances directly in the liquid state had for its object the hydrogenation of liquid fats and was made in 1902–1903.[1] Then followed the method of Ipatief based on the use of nickel at 250 to 400° in the presence of hydrogen compressed to more than 100 atmospheres, and at almost the same time the method

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[1] LEPRINCE and SIEVKE, *German patent*, 141,029 (1903). — NORMAN, *English patent*, 1515 of 1903. *Chem. Cent.*, 1903 (1), 1199.

of Paal, relying on the use of colloidal metals (platinum or palladium) acting at near the ordinary temperature, and then in 1908, the method of Willstätter which depends on the use of platinum black.

We shall take up first the methods using the precious metals, then those employing the common metals whether at high pressures of hydrogen or at pressures near the atmospheric.

543. Except the process of Ipatief, which, on account of the high pressures used, demands an entirely special outfit, the various methods of hydrogenation in liquid medium employ apparatus of the same kind, though they may vary much in forms and dimensions. The main thing is a working vessel containing the liquid to be hydrogenated, either alone or dissolved in a suitable solvent and mixed with the solid catalyst. This recipient, which must be capable of being kept at known temperatures, is mounted on a mechanical shaker capable of assuring the best possible contact between liquid, catalyzer, and hydrogen. It is kept in communication with a cylinder of compressed hydrogen which can be introduced from time to time under known pressures, or if the hydrogenation is to be carried on at atmospheric pressure, the recipient communicates continuously with a hydrogen gasometer, the graduations of which enable us to follow the course of the reaction and to determine its end.

I. — METHOD OF PAAL

544. The methods of preparing *colloidal platinum* and *palladium,* such as are used in the method of Paal, have been given above (67 to 71). The amounts of these metals to be used are not over 16 to 50% of the weight of the substance to be hydrogenated, and can, according to Paal, be reduced to from 0.5 to 1% for colloidal palladium or to 1 to 2% for colloidal platinum.[2]

Use of Colloidal Palladium

545. **Reductions with Simultaneous Fixation of Hydrogen.** *Nitro* compounds are readily changed into *amino* compounds. Thus *nitrobenzene* is easily transformed into *aniline,* particularly at 65–85°.[3]

Nitroacetophenone gives *aminoacetophenone.*[4]

The halogen of chlorine or bromine derivatives may be readily replaced by hydrogen when a current of hydrogen is passed through

[2] Paal, *German patent,* 298,193, 1913, — *Chem. Cent.,* 1917 (2), 145.
[3] Paal and Amberger, *Berichte,* 38, 1406 (1906).
[4] Skita and Meyer, *Berichte,* 45, 3579 (1912).

the compound containing colloidal palladium and boiling under reflux. Thus we obtain *benzene* from *brombenzene*. This reduction works well with *o.chlor-benzoic acid, o.chlorcinnamic acid, chlorcrotonic acid,* and *chlorcaffeine,* etc., without any other change in the molecule.[5]

546. Fixation of Hydrogen by Addition. The ethylene double bond is readily hydrogenated.

Ethylene is easily transformed into *ethane.*[6]

Styrene gives *ethyl-benzene.*

Bromstyrene is simultaneously saturated and dehalogenated to *ethyl-benzene.*[7]

1,10–Diphenyl-decadiene(1,9) furnishes *1,10–diphenyl-decane.*[8]

Mesityl oxide, treated in alcohol solution with the metal prepared by means of gum arabic, changes into *methyl-isobutyl-ketone.*[9]

α-Methyl-β-ethyl-propenal, hydrogenated under the same conditions under 2 atmospheres pressure of hydrogen, gives chiefly the saturated aldehyde, *α-methyl-valeric aldehyde,* accompanied by a small amount of the unsaturated alcohol *α-methyl-pentenyl alcohol.*[10]

Crotonic, isocrotonic, and *tetrolic acids* are transformed into the corresponding saturated acids.[11]

Fumaric acid in an hour and a half, and *maleïc acid* in seven hours are changed into *succinic acid. Oleïc acid* gives a 60% yield of *stearic acid* in 43 minutes.

Cinnamic acid is changed into *phenylpropionic acid.*[12]

Cinnamic aldehyde, dissolved in 20 parts of alcohol, is transformed into *phenylpropionic aldehyde.*[13]

Isopropylidene-cyclopentanone adds H_2 to form *isopropyl-cyclopentanone:*[14]

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C:C \begin{array}{c} \diagup CO - CH_2 \\ | \\ \diagdown CH_2 - CH_2 \end{array} \rightarrow \begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} CH.CH \begin{array}{c} \diagup CO - CH_2 \\ | \\ \diagdown CH_2 - CH_2 \end{array}$$

[5] ROSENMUND and ZETSCHE, *Berichte,* **51,** 579 (1918).

[6] PAAL and HARTMANN, *Berichte,* **48,** 984 (1915).

[7] BORSCHE and HEIMBÜRGER, *Berichte,* **48,** 452 (1915).

[8] BORSCHE and WOLLEMANN, *Berichte,* **44,** 3185 (1911).

[9] WALLACH, *Nach. Ges. der Wiss. Gottingen,* **1910,** 517. — SKITA, *Berichte,* **48** 1486 (1915).

[10] SKITA, *Berichte,* **48,** 1486 (1915).

[11] BÖESEKEN, VAN DER WEIDE and MOM, *Rec. Trav. Chim. Pays Bas.,* **35,** 260 (1915).

[12] PAAL and GERUM, *Berichte,* **41,** 2273 and 2277 (1908).

[13] SKITA, *Berichte,* **48,** 1691 (1915). — BÖESEKEN, VAN DER WEIDE and MOM, *Rec. Trav. Chim. Pays-Bas,* **35,** 260 (1916).

[14] WALLACH, *Annalen,* **394,** 362 (1912).

547. In the case of diethylene compounds, if the double bonds are consecutive, both are hydrogenated simultaneously but if they are separated by more than one carbon atom, they are hydrogenated successively.

Thus *phorone* gives first *dihydrophorone* and then *valerone*.

Dibenzylidene-acetone, C_6H_5 . CH : CH . CO . CH : CH . C_6H_5, can give first *benzyl-benzylidene-acetone*, C_6H_5 . CH : CH . CO . CH_2 .- CH_2 . C_6H_5, and then *dibenzyl-acetone*.[15]

548. The *acetylene* triple bond can be saturated in two steps. *Acetylene* itself gives ethylene chiefly, up to 80%.[16]

Phenyl-acetylene in acetic acid solution gives *styrene* and then *ethyl-benzene*.[17]

Tolane yields *stilbene* and then *dibenzyl*. *Diphenyl-diacetylene* passes into $\alpha\gamma$-*diphenyl-butadiene* $\alpha\gamma$, then into $\alpha\gamma$-*diphenyl-butane*.[17]

Phenylpropiolic acid, C_6H_5 . C : C . COOH, gives a poor yield of *cinnamic acid*, C_6H_5 . CH : CH . CO_2H, and does not go into phenyl-propionic.[18]

2,5-*Dimethyl-hexine*(3)-*diol*(2,5) adds only H_2 to give the *ethylene-diol*, and the same is true of 1,4-*diphenyl-butine*(2)-*diol*(1,4)[19] and of *dimethyl-diethyl-butine-diol*,[20] while *dimethyl-diphenyl-butine-diol* gives, in succession, the ethylene *glycol* and the saturated *glycol*.[21] On the contrary, 2-*methyl-4-phenyl-butine*(3)-*ol*(2), $(CH_3)_2C(OH)$. C   C . C_6H_5, adds 2H_2 immediately to give the saturated alcohol.[22]

$$Dimethyl\text{-}octine\text{-}diol, \quad \begin{matrix} CH_3.CH_2 \\ \diagdown \\ CH_3 \diagup \end{matrix} C(OH).C \vdots C.C(OH) \begin{matrix} \diagup CH_2.CH_3 \\ \diagdown CH_3 \end{matrix},$$

hydrogenated in alcohol solution, adds H_2 to form *dimethyl-octene-diol*.[23]

In the hydrogenations of these acetylene glycols, the speed of the reaction is usually proportional to the amount of catalyst present,

[15] PAAL, *Berichte*, **45**, 2221 (1912).

[16] PAAL and HOHENEGGER, *Berichte*, **48**, 275 (1915). — PAAL and SCHWARZ, *Berichte*, **48**, 1202 (1915).

[17] KELBER and SCHWARZ, *Berichte*, **45**, 1951 (1912).

[18] PAAL and SCHWARZ, *Berichte*, **51**, 640 (1918).

[19] ZALKIND, *J. Russian Phys. Chem. Soc.*, **45**, 1875 (1914), *C. A.*, **8**, 1419.

[20] ZALKIND and MISS MARKARYAN, *J. Russian Phys. Chem. Soc.*, **48**, 538 (1916), *C. A.*, **11**, 584.

[21] ZALKIND and KVAPISHEVSKII, *J. Russian Phys. Chem. Soc.*, **47**, 688 (1915), *C. A.*, **9**, 2511.

[22] ZALKIND, *J. Russian Phys. Chem. Soc.*, **47**, 2045 (1915), *C. A.*, **10**, 1355.

[23] ZALKIND and MISS MARKARYAN, *J. Russian Phys. Chem. Soc.*, **48**, 538 (1916), *C. A.*, **11**, 584.

but sometimes it is independent of the amount of catalyst, contrary to all predictions.

549. The transformation of aldehydes and ketones into alcohols can be effected, but with difficulty.

Benzaldehyde is partially reduced to *benzyl alcohol.*[24]

Phenyl-acetaldehyde is regularly hydrogenated to the corresponding alcohol.

With hydrogen at one atmosphere pressure, *phorone* is hydrogenated to *di-isobutyl-carbinol,* but under half an atmosphere, the reduction stops at *valerone.*[24]

In acetic acid solution, *mesityl oxide* is hydrogenated to methyl-isobutyl-carbinol, but in alcohol, as stated above, the reaction stops at the ketone.[25] The saturated alcohol is also obtained by working under 5 atmospheres pressure.[24]

550. *Hydroxy-methylene* derivatives containing the group $\diagup C : CHOH$, are changed into methyl derivatives $\diagup CH . CH_3.$ [26]

551. *Benzoic acid* furnishes *hexahydrobenzoic.*[27]

552. *Carvone* is transformed into *tetrahydrocarvone.* There is addition of hydrogen to the double bonds of *pinene,* which, under 2 atmospheres pressure, gives *pinane,* of *camphene* which passes to *camphane,* melting at 53°,[28] of *eucarvone,* of α- and β-*terpineols,* of *thujone,* of *isothujone,* of *methylheptenone,* of *cyclohexenone,* etc.[29] Likewise *pulegone* is changed to *menthone.*

553. *Naphthalene* is reduced to *decahydronaphthalene.*[30]

554. *Azobenzene,* in alcohol solution under 2 atmospheres pressure of hydrogen, is reduced to *hydrazobenzene* in five minutes and then into *aniline* in 4.5 hours. *Orange No. 3* is immediately decolorized under these conditions.[30]

The α- and β-*ionones* are transformed into the odorless dihydro– and then into the tetrahydroionones.[31]

555. *Quinidine* gives *dihydroquinidine,* melting at 165°. *Cinchonidine* adds H_2 to form the dihydro– melting at 229°.[32] *Cinchonine* adds H_2 to form *cinchotine.*[33]

[24] Skita and Ritter, *Berichte* **43**, 3393 (1910).

[25] Skita, *Berichte,* **48,** 1486 (1915).

[26] Kötz and Schaeffer, *J. prakt. Chem.* (2), **88,** 604 (1913).

[27] Skita and Meyer, *Berichte,* **45,** 3587 (1912).

[28] Skita and Meyer, *Berichte,* **45,** 3579 (1912).

[29] Wallach, *Annalen,* **336,** 37 (1904).

[30] Skita, *Berichte,* **45,** 3312 (1912).

[31] Skita, Meyer and Bergen, *Berichte,* **45,** 3312 (1912).

[32] Skita and Nord, *Berichte,* **45,** 3316 (1912).

[33] Paal, *German patent,* 223,413.

Pyridine is changed to *piperidine* and *quinoline* to *decahydro-quinoline.*[27]   *Diacetyl-morphine* furnishes the dihydro– and *piperine, tetrahydropiperine.*[28]

Strychnine, dissolved in dilute nitric acid under 2 atmospheres pressure of hydrogen, gives the dihydro–, but under 3 atmospheres, tetrahydrostrychnine, while *brucine* always gives its dihydro–.[34]

Colchicine furnishes *tetrahydrocolchicine.*[35]

Egg *lecithine,* dissolved in absolute alcohol, gives *hydrolecithine.*[36]

Use of Colloidal Platinum

556. Colloidal platinum, prepared according to one of the methods given in Chapter II (67 to 71), can be substituted for colloidal palladium and gives results but little different.

According to Paal and Gerum its activity is less.[37]   According to Fokin, on the contrary, the platinum is three times as active and much more apt to hydrogenate the aromatic nucleus.[38]   The velocity of the hydrogenation increases rapidly with the amount of the metal employed.[39]

557. The reduction of *nitro*-derivatives into *amino*- is readily carried out with *nitrobenzene* which gives *aniline* and with *nitroacetophenone* which yields *aminoacetophenone.*[40]

558. The addition of hydrogen to double and triple bonds takes place easily even with many complex rings.

Ethylene is transformed to ethane but less rapidly than by colloidal palladium, the action being proportional to the amount of platinum used.[41]

Amylene is changed to *pentane, oleïc* and *linoleïc acids* into *stearic* and *crotonic, maleïc, aconitic, sorbic, citraconic,* and *itaconic acids* are changed into the corresponding saturated acids, while *allyl alcohol* gives *propyl alcohol.*[38]

Acetylene is reduced to a mixture of ethylene and ethane.[42]

559. *Heptaldehyde,* hydrogenated by the aid of colloidal platinum prepared by the germ method, is changed to heptyl alcohol.[43]

[34] Skita and Paal, *German patent,* 230,724, *C.,* 1911 (1), 522.
[35] Hoffmann — La Roche & Co., *German patent,* 279,999, *C.,* 1914 (2),1214.
[36] Paal and Oehme, *Berichte,* 46, 1297 (1913).
[37] Paal and Gerum, *Berichte,* 40, 2209 (1907) and 41, 2273 (1908).
[38] Fokin, *J. Russian Phys. Chem. Soc.,* 40, 276 (1908).
[39] Fokin, *Z. Angew. Chem.,* 22, 1492 (1909).
[40] Skita and Meyer, *Berichte,* 45, 3579 (1912).
[41] Paal and Schwarz, *Berichte,* 48, 994 (1915).
[42] Paal and Schwarz, *Berichte,* 48, 1202 (1915).
[43] Skita and Meyer, *Berichte,* 45, 3589 (1912).

a-Methyl-β-ethyl-propenal, treated in acetic acid solution, is changed completely into *a-methyl-pentanol*.

Mesityl oxide, in water solution, goes to *methyl-isobutyl-ketone*, but in acetic acid solution, into *methyl-isobutyl-carbinol*.[44]

560. The aromatic nucleus is hydrogenated more or less readily. With the metal prepared by the germ method, *benzene* is transformed into *cyclohexane*.

Toluene, in acetic acid solution under 2 atmospheres pressure, is changed to *methyl-cyclohexane* and *benzoic acid* into *hexahydrobenzoic*.[45]

Cinnamic aldehyde is transformed into *phenylpropionic aldehyde* in the cold. In acetic acid solution *phenylpropyl alcohol* is obtained mixed with a little *propyl-benzene*, while with a larger amount of the catalyst and a pressure of 3 atmospheres, *cyclohexyl-propyl alcohol* is obtained. Under the same conditions, in acetic acid solution, *benzyl-aniline* furnishes *hexahydrobenzyl-aniline* accompanied by *cyclohexyl-amine* and *methyl-cyclohexane*.[46]

Phenylacetaldehyde gives the corresponding alcohol with a little ethyl-benzene, cyclohexanol, cyclohexanone, and cyclohexane.

Benzaldehyde gives *toluene* and *methyl-cyclohexane* along with *benzyl alcohol*.

Benzophenone yields *dicyclohexyl-methane* at 60°.

a and *β-Ionones*, in acetic acid solution, furnish *trimethyl-hydroxybutylcyclohexane*.[47]

Caryophyllene, $C_{15}H_{24}$, adds H_2 in methyl alcohol solution.[48]

561. With colloidal platinum, prepared with gum arabic, we can obtain *piperidine* from *pyridine*.[45]

The addition of $3H_2$ takes place with various homologs of pyridine, hydrogenated in acetic acid solution under atmospheric pressure or under 2 or 3 atmospheres.[49]

The *pyridine-carbonic* acids are transformed into *piperidinic* acids.[50]

Quinoline gives, in turn, *tetrahydro-* and then *decahydroquinoline*.[45]

Diacetyl-morphine adds H_2 and *cinchonine* yields *hexahydrocinchonine*.[51]

[44] Skita, *Berichte*, **48**, 1486 (1915).
[45] Skita and Meyer, *Berichte*, **45**, 3589 (1912).
[46] Skita, *Berichte*, **48**, 1685 (1915).
[47] Skita, *Berichte*, **48**, 1486 (1915).
[48] Deussen, *Annalen*, **388**, 136 (1912).
[49] Skita and Brunner, *Berichte*, **49**, 1597 (1916).
[50] Hess and Liebbrandt, *Berichte*, **50**, 385 (1917).
[51] Skita and Brunner, *Berichte*, **49**, 1597 (1916).

II. METHOD OF WILLSTÄTTER

562. The process consists in submitting to a current or to an unlimited amount of an atmosphere of hydrogen gas, the substance dissolved in a suitable vehicle and intimately mixed by means of constant agitation with the *platinum* or *palladium black*. It was employed first by Fokin, who transformed in this way *oleïc acid* dissolved in ether into stearic acid by a current of hydrogen in the cold with palladium or platinum black as catalyst.[52]

But Willstätter is the one who has generalized this method by applying it to various uses.

Platinum black prepared according to the method of Loew (62) serves best.[53] *Palladium black* can also be used: it is prepared by reducing *palladous chloride* with formaldehyde in the presence of caustic soda.[54] But it is not so desirable as platinum black.

The substance dissolved in ether or in any other inert solvent is treated with the *platinum black* and is put into a flask which is continually agitated by a mechanical shaking machine and which communicates with a gasometer filled with hydrogen. According to circumstances, quite different amounts of platinum black are used, varying from 3 to 33 % of the weight of the substance.

Dilution of the material is not indispensable to the success of the method.

Use of Platinum Black

563. Willstätter has called attention to this quite unexpected fact, that in certain cases hydrogenation by means of platinum black is not possible unless it has been previously charged with a certain proportion of oxygen.

In most cases, platinum black containing oxygen or free from oxygen may be used indifferently, as in the hydrogenation of benzene to cyclohexane; on the contrary, the hydrogenation of pyrrol requires platinum black absolutely free from oxygen. On the other hand, the decomposition of hydrazine demands that the platinum black that is to be used be previously aerated.[55]

The aeration of the platinum black is indispensable for the hydrogenation in acetic acid solution of *phthalic* and *naphthalic anhydrides* and the reaction does not continue unless the apparatus is opened

[52] Fokin, *J. Russian Phys. Chem. Soc.*, **39**, 607 (1907).
[53] Somewhat improved method Willstätter and Waldschmidt-Leitz, *Berichte*, **54**, 121 (1921). — E. E. R.
[54] Breteau, *Div. méth. d'hydr. app. au Phénant*, Paris, 1911, p. 25.
[55] Purgotti and Zanichelli, *Gaz. Chim. Ital.*, **34** (1), 57 (1904).

from time to time for the aeration of the black. Oxygen appears to play an active part in the hydrogenation which is indicated by the products obtained. For phthalic anhydride the products are, *hexahy-*

drophthalid, C_6H_{10}⟨$\overset{\text{CH}_2}{\underset{\text{CO}}{}}$⟩$O$, *o.hexahydrotoluic* and *hexahydrophthalic*

acids, and for naphthalic acid, *tetrahydronaphthalid, hexahydronaph-thalid, decahydroacenaphthene,* $C_{12}H_{20}$, and *tetrahydro-methyl(1) naphtha-lene-carbonic acid(8).*

The influence of these anhydrides on the conditions of hydrogenation can effect even the hydrogenation of the dibasic acids themselves; the presence of the anhydrides prevents this from taking place unless the platinum be aerated. *Isophthalic* acid, which usually contains traces of the anhydride, can not be hydrogenated except with aerated platinum.[56] [57]

564. **Nitro Compounds.** The reduction of *nitro* or *nitroso* compounds to *amino* is readily effected by 1 cg. of platinum black to 1 g. of the material dissolved in ether or acetone. A few minutes are sufficient for complete reduction; thus *p.nitrotoluene* is changed to *p.toluidine, 1-nitrosonaphthol(2),* into *aminonaphthol.* But the *nitroso-terpenes* are changed quantitatively into the corresponding hydroxylamines.[58]

565. **Ethylene Double Bonds.** These are readily saturated. *Amylene* is changed to *pentane.*

ω-*Nitrostyrene,* dissolved in absolute alcohol or in glacial acetic acid, adds a single atom of hydrogen, two molecules combining[59]:

$$C_6H_5.CH : CH.NO_2$$
$$C_6H_5.CH : CH.NO_2$$
$$\longrightarrow$$
$$C_6H_5.CH.CH_2.NO_2$$
$$C_6H_5.CH.CH_2.NO_2$$

Oleïc alcohol is readily transformed into *octadecyl alcohol, ethyl oleate* quantitatively into *ethyl stearate,* and *erucic alcohol* into *docosyl alcohol.*

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[56] WILLSTÄTTER and JACQUET, *Berichte,* **51,** 767 (1918).

[57] In a more recent article WILLSTÄTTER and WALDSCHMIDT-LEITZ [*Berichte,* **54,** 113 (1920)] show that the presence of oxygen in the platinum black is necessary in all cases. This oxygen is gradually used up by the hydrogen during the process of hydrogenation. With ethylene compounds the addition of the hydrogen is so extremely rapid that the desired hydrogenation may be accomplished before the catalyst becomes inactive by loss of its oxygen but if the hydrogenation is slow, the catalyst may require revivification by aeration at intervals during the process. In this respect palladium black and even nickel act similarly to platinum black. — E. E. R.

[58] CUSMANO, *Lincei,* **26** (2), 87 (1917).

[59] SONN and SCHNELLEMBERG, *Berichte,* **50,** 1913 (1917).

Phytene, $C_{20}H_{40}$, gives *phytane*, $C_{20}H_{42}$; *phytol*, $C_{20}H_{39}OH$, *dihydrophytol*, $C_{20}H_{41}OH$, slowly but with a good yield. *Geraniol* (416) is hydrogenated only slowly and gives the corresponding saturated alcohol at the end of several days.[60]

Linalool furnishes *2, 6-dimethyl-octanol(6)*.[61]

Safrol and *isosafrol* are hydrogenated in two hours to *dihydrosafrol*. Likewise *eugenol* and *isoeugenol* pass into *isopropyl-guaiacol*.[62]

Piperonal-acetone and *dipiperonal-acetone* are transformed into the saturated ketones.[63]

Cholesterine, in ether solution with one third its weight of platinum black, is changed into *dihydrocholesterine* in two days.[64]

Oleïc acid gives *stearic* and *ethyl oleate* yields *ethyl stearate*.[65]

566. **Acetylene Triple Bonds.** The *acetylene glycols* of the formula, $RR' : C(OH).C \vdots C.C(OH) : RR'$, give the corresponding saturated glycols and also certain amounts of the alcohols, $RR' : C(OH)CH_2.-CH_2.CH_2 : RR'$.[64] Thus *2, 5-dimethyl-hexine(3)diol(2, 4)* furnishes the saturated glycol.[66]

Dimethyl-diethyl-butine-diol, which adds only H_2 with colloidal palladium (548), takes up $2H_2$ with platinum black.[67]

Dimethyl-diphenyl-butine-diol can add H_2 and then $2H_2$ by steps.[68]

Octadi-ine-diol(1, 8), $HOH_2C.C \vdots C.CH_2.CH_2.C \vdots C.CH_2OH$, hydrogenated at 70° in alcohol solution, gives a mixture of *octane-diol (1, 8)* and *n.octyl alcohol*.[69]

Octadi-ine-dioic acid, $HO_2C.C \vdots C.CH_2.CH_2.C \vdots C.CO_2H$, dissolved in a mixture of alcohol and ether, furnishes *suberic acid* in four days.[70]

567. **Aldehydes and Ketones.** *Aldehyde* and *ketone* groups can be regularly transformed into the corresponding alcohol groups. *Crotonic aldehyde*, in anhydrous ether, is changed in eleven hours into a mixture of 70 % *butyric aldehyde* and 30 % *butyl alcohol*.[71]

[60] WILLSTÄTTER and MAYER, *Berichte*, **41**, 1475 (1908).
[61] BARBIER and LOCQUIN, *Compt. rend.*, **158**, 1555 (1914).
[62] FOURNIER, *Bull. Soc. Chim.* (4), **7**, 23 (1910).
[63] VAVON and FAILLEBIN, *Compt. rend.*, **169**, 65 (1919).
[64] WILLSTÄTTER and MAYER, *Berichte*, **41**, 2199 (1908).
[65] DUPONT, *Compt. rend.*, **156**, 1623 (1913).
[66] ZALKIND, *J. Russian Phys. Chem. Soc.*, **45**, 1875 (1914), *C. A.*, **8**, 1419.
[67] ZALKIND and MISS MARKARYAN, *J. Russian Phys. Chem. Soc.*, **48**, 538 (1916), *C. A.*, **11**, 584.
[68] ZALKIND and KVAPISHEVSKII, *J. Russian Phys. Chem. Soc.*, **47**, 688 (1915), *C. A.*, **9**, 2511.
[69] LESPIEAU, *Compt. rend.*, **158**, 1187 (1914).
[70] LESPIEAU and VAVON, *Compt. rend.*, **148**, 1335 (1909).
[71] FOURNIER, *Bull. Soc. Chim.* (4), **7**, 23 (1910).

Acetone is changed to *isopropyl alcohol* in water solution and *methyl-ethyl-ketone* is changed into *methyl-ethyl-carbinol* in 12 hours. *Diethyl* and *dipropyl-ketones* are similarly reduced.

The transformation into the alcohol is more readily effected with *cyclopentanone* dissolved in 5 volumes of ether, with *cyclohexanone* and with the *methyl-cyclohexanones*.

Mesityl oxide gives first *methyl-isobutyl-ketone* and then *methyl-isobutyl-carbinol*.

In ether solution, *phorone* yields *diisobutyl-ketone*, while in acetic acid it gives *diisobutyl-carbinol*.

Citral in ether solution gives a mixture of *2, 6-dimethyl-octane* and *2, 6-dimethyl-octanol (8)*.[72]

Menthone yields *menthol* and *pulegone* gives *pulegomenthol*.[73]   *Carvone* with 20 % of platinum black takes up in succession, H_2, $2H_2$, $3H_2$ to form *carvotanacetone, tetrahydrocarvone* and finally *carvomenthol* slowly.[74]

568. **Aromatic aldehydes** are transformed almost quantitatively into alcohols, which is a valuable reaction since other methods give hydrocarbons (388). With 10 g. of *black* a gram molecule can be hydrogenated in a few hours. This can be done with *benzaldehyde, methyl-salicylic, benzoyl-salicylic,* and *anisic aldehydes, vanilline* and its *methyl, ethyl, acetyl,* and *benzoyl* derivatives, *piperonal,* which gives the alcohol melting at 54°, and *cinnamic aldehyde,* which yields *phenyl-propyl alcohol*.[75]

At 70° *anisaldehyde* gives *anisalcohol* but at 97° it is polymerized.

On the contrary, *acetophenone* takes up 10 atoms of hydrogen at once to form *ethyl-cyclohexane*.[76]

569. **Aromatic Nucleus.** *Aromatic* compounds are completely hydrogenated to cyclohexane derivatives on the condition that they are perfectly pure. Traces of impurities, particularly sulphur compounds, hinder the reaction.[77]

Toluene and the *xylenes* are hydrogenated more readily than benzene, and higher homologs still more readily. *Butyl-benzene, amyl-benzene, hexyl-benzene, octyl-benzene,* etc., up to *pentadecyl-benzene* are readily changed in acetic acid solution into the corresponding cyclohexane derivatives.[78]

Durene furnishes *hexahydrodurene*.

[72] Vavon, *Ann. Chim.* (9), 1, 144 (1914).
[73] Vavon, *Compt. rend.,* 155, 287 (1912).
[74] Vavon, *Compt. rend.,* 153, 68 (1911).
[75] Vavon, *Compt. rend.,* 154, 359 (1912).
[76] Vavon, *Compt. rend.,* 155, 287 (1912).
[77] Willstätter and Hatt, *Berichte,* 45, 1471 (1912).
[78] Halse, *J. prakt. Chem.* (2), 92, 40 (1915).

Styrene gives *ethyl-cyclohexane*;[79] and *phenol, cyclohexanol.*[77]

Eugenol adds $4H_2$ to form *propyl-methoxy-cyclohexanol.*[80]

Aniline produces chiefly *dicyclohexyl-amine* with only 10 % of *cyclohexyl-amine*. *Chlortoluene* is transformed into *methyl-chlorcyclohexane.*[77]

In ether solution, *benzoic acid* is slowly changed to *hexahydrobenzoic acid* without intermediate products.[81]

In acetic acid solution, *p.aminobenzoic acid* is quantitatively reduced to *p.aminocyclohexane-carbonic* acid and *hydroxybenzoic* acid is similarly hydrogenated.[82]

We have seen above (563) that phthalic anhydride can be hydrogenated by means of platinum black aerated from time to time. The ordinary method serves well for *phthalimide* which gives as the sole product, *hexahydrophthalimide :*[83]

$$CH_2.CH_2.CH_2.CO$$
$$CH_2.CH_2.CH_2.CO \Big\rangle NH.$$

570. Terpenes. *Limonene*, in ether solution with 25 % of its weight of platinum, adds H_2 in 30 minutes in the cold to form *carvomenthene*, boiling at 175°, and then an additional H_2 in 65 minutes to form *menthane.*[84]

Pinene, 500 g. with 15 g. platinum, absorbs hydrogen rapidly, 60 l. per hour at the start, and at the end of 24 hours is entirely transformed into *dihydropinene*, boiling at 166° (477). *Camphene* gives a solid *dihydrocamphene* melting at 87°.[85]

α-Thujene, $C_{10}H_{16}$, which by the method of Sabatier and Senderens yields menthane (478), is totally transformed by platinum black and hydrogen under 25 to 50 atmospheres in two days into *thujane*, $C_{10}H_{18}$, boiling at 157°, the inner ring remaining intact. Similar transformations take place with *β-thujene* and with *sabinene.*[86]

Isoamyl-carvol adds $2H_2$ to give the corresponding saturated alcohol.[87]

The sesquiterpenes, $C_{15}H_{24}$, as well as their ketone and alcohol derivatives, add 4 or 6 atoms of hydrogen.

[79] WILLSTÄTTER and KING, *Berichte*, **46**, 527 (1913).

[80] MADINAVEITIA and BLANES, *Soc. Espan. Fis. Quim.*, **10**, 381 (1913), *C. A.*, **7**, 3500.

[81] WILLSTÄTTER and MAYER, *Berichte*, **41**, 1475 (1908).

[82] HOUBEN and PEAU, *Berichte*, **49**, 2294 (1916).

[83] WILLSTÄTTER AND JACQUET, *Berichte*, **51**, 767 (1918).

[84] VAVON, *Bull. Soc. Chim.* (4), **15**, 282 (1914).

[85] VAVON, *Compt. rend.*, **149**, 997 (1909) and **152**, 1675 (1911).

[86] TCHOUGAEFF and FOMIN, *Compt. rend.*, **151**, 1058 (1910).

[87] SEMMLER, JONAS and OELSNER, *Berichte*, **50**, 1838 (1917).

Thus *isozingiberene*,[88] *eudesmene*,[89] and *ferulene*,[90] take up 2H$_2$. The same is true of *doremone*, $C_{15}H_{26}O$, which gives *tetrahydrodoremone* without alteration of the ketone group and of *doremol* which forms the saturated alcohol. *Farnesol*, $C_{15}H_{26}O$ adds 3H$_2$.[90]

Betulol, $C_{15}H_{24}O$, adds 2H$_2$ to form the alcohol, $C_{15}H_{28}O$, when it is hydrogenated in anhydrous ether solution.[91]

571. Complex Rings. *Cyclo-octenone* is changed to *cyclo-octanone* by 10 % of its weight of black. *Cyclo-octatriene* and *cyclo-octatetrene*,

$$CH : CH . CH : CH$$
$$\hspace{3em} \cdot \hspace{3em} \cdot \hspace{0.5em} , \text{ are transformed into } \textit{cyclo-octane.}[92]$$
$$CH : CH . CH : CH$$

In the hydrogenation of the latter, the first three H$_2$ are fixed with about the same velocity, while the last H$_2$ is added only about half so fast.[93]

Naphthalene adds hydrogen rapidly to form the *dihydro-* and then the *tetrahydro-* and finally, more slowly, *decahydro-naphthalene*.[94]

Phenanthrene, dissolved in ether, gives *dihydro-phenanthrene* (melting at 94°), in two days in the cold, or in 8 hours at the boiling point of the ether.[95] However, Breteau failed to obtain any hydrogenation in cyclohexane solution.[96]

Santonine yields *tetrahydro-santonine* when hydrogenated in glacial acetic acid.[97] Sodium santonate takes up the same amount of hydrogen to form sodium tetrahydrosantonate.[98]

Pyrrol adds 2H$_2$ to form *pyrrolidine*.[99]

Indol, in glacial acetic acid, yields *octahydro-indol*, an alkaline liquid with a disagreeable odor boiling at 182°, accompanied by a little *dihydro-indol*.[100]

572. *Quinine sulphate* is completely hydrogenated in dilute sulphuric acid solution by hydrogen under a pressure of more than an atmosphere to *dihydroquinine sulphate*, the hydrogenation being con-

[88] SEMMLER and BECKER, *Berichte*, **46**, 1814 (1913).

[89] SEMMLER and RISSE, *Berichte*, **46**, 2303 (1913).

[90] SEMMLER, JONAS and ROENISCH, *Berichte*, **50**, 1823 (1917).

[91] SEMMLER, JONAS and RICHTER, *Berichte*, **51**, 417 (1918).

[92] WILLSTÄTTER and WASER, *Berichte*, **44**, 3434 (1911).

[93] WILLSTÄTTER and HEIDELBERGER, *Berichte*, **46**, 517 (1913).

[94] WILLSTÄTTER and HATT, *Berichte*, **45**, 1471 (1912). — WILLSTÄTTER and KING, *Ibid.*, **46**, 527 (1913).

[95] SCHMIDT and FISCHER, *Berichte*, **41**, 4225 (1908).

[96] BRETEAU, *Méth. d'hydrog. app. au Phénant*, Paris, 1911, p. 20.

[97] ASAHINA, *Berichte*, **46**, 1775 (1913).

[98] CUSMANO, *Lincei*, **22**, 507 (1913).

[99] WILLSTÄTTER and HATT, *Berichte*, **45**, 1371 (1912).

[100] WILLSTÄTTER and JACQUET, *Berichte*, **51**, 767 (1918).

tinued till the solution does not decolorize potassium permanganate.[101]
Dihydromorphine and *dihydrocodeïne* can be obtained in the same
way.[102]

Use of Palladium Black

573. The use of palladium black [103] immersed in the liquid appears
to be usually less advantageous than the use of platinum black. How-
ever, it has led to some remarkable results, such as the reduction of
carbonates to formates.

574. **Reduction without Addition of Hydrogen.** The most important
reaction is the synthesis of formates by the reduction of *bicarbonates:*

$$KHCO_3 + H_2 = HCO_2K + H_2O.$$

This requires a high pressure and a temperature around 70°.

In a silver plated bomb, 10 g. potassium bicarbonate, 200 cc. water,
and 1.5 g. palladium black are placed with hydrogen at 60 atmospheres.
After heating for 24 hours to 70°, 74.7 % of the salt is changed to
formate.

The reaction takes place without catalyst, but extremely slowly,
only 0.6 % of formate being produced in 24 hours.

The potassium bicarbonate can be replaced by sodium borate, the
bomb then being filled with equal volumes of carbon dioxide and hy-
drogen under 60 atmospheres.[104]

The reaction can be carried out without the presence of the alkali
salt, by maintaining a mixture of carbon dioxide and hydrogen under
high pressure in the presence of water and palladium black. By working
at 20° and under a pressure of 110 atmospheres a 1 % solution of formic
acid is obtained.[105]

575. **Reduction of Acid Chlorides.** Another reaction which is
peculiar to palladium black is the reduction of *acid chlorides* to *aldehydes*:

$$R.COCl + H_2 = R.CHO + HCl.$$
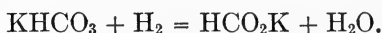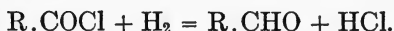
The acid chloride, dissolved in a hydrocarbon, is submitted to hy-
drogenation in the presence of palladium black precipitated on barium
sulphate.

Benzoyl chloride gives benzaldehyde with a yield of 97 %; *butyryl*

[101] Verein, Chininfabr. Zimmer & Co., *English patent* 3,948 of 1912.

[102] *German patent* 260,233.

[103] Preparation — Willstätter and Waldschmidt-Leitz, *Berichte*, **54**, 123
(1921). — E. E. R.

[104] Bredig and Carter, *Berichte*, **47**, 541 (1914).

[105] Bredig and Carter, *English patent*, 9,762 of 1915; *J. S. C. I.*, **34**, 1207
(1915).

chloride furnishes 50 % of the aldehyde and *stearyl chloride* is reduced to its *aldehyde*.[106]

576. Nitro Compounds. The reduction of *nitro* to amino compounds is difficult to carry out with palladium, but *nitrobenzene* does give *aniline* on prolonged contact with an excess of hydrogen and palladium black in alcohol solution.[107]

577. Ethylene and Acetylene Bonds. *Oleïc acid*, in ether solution, is slowly transformed to stearic acid, the reduction being rapid when it is carried on at a higher temperature and with hydrogen under pressure. The same is true for the *esters* of *oleïc acid* and this is the basis for the industrial use of palladium black in the hardening of liquid fats (946).

Vinyl-trimethylene, $CH_2 : CH . CH \Big\langle \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}$, treated in the cold with

hydrogen under 35 atmospheres in the presence of palladium chloride, which is reduced, yields ethyl-trimethylene.[108]

The acetylene glycols of the type, $RR' : C(OH).C : C.C(OH) : RR'$, yield mainly the saturated hydrocarbons, $RR' : CH.CH_2.CH_2-CH : RR'$.[109]

Eugenol stops with the formation of *dihydroeugenol*,[110] the ring not being hydrogenated as with platinum black (569).

578. Aromatic Nucleus. The hydrogenation of the aromatic nucleus is not usually effected by palladium black, but the hydrogenation of *hexahydroxybenzene* to *inosite* at 50–55° may be mentioned. The inosite formed melts at 218° as does natural inosite.[111]

579. *Phenanthrene* is hydrogenated, in cyclohexane solution, by half its weight of the black to *tetrahydrophenanthrene*.[112]

Use of other Metals of Platinum Group

580. Ruthenium Black. The black prepared by formaldehyde and ruthenium chloride solution has a catalytic activity inferior to that of platinum.

If 0.05 g. of this black is added to 0.5 g. *cinnamic acid* in 2 cc. glacial acetic acid, *phenyl-propionic* acid is formed in 8 hours without

[106] ROSENMUND, *Berichte*, **51**, 585 (1918).

[107] GERUM, *Inaug. Dissertation, Erlangen*, 1908.

[108] FILIPPOV, *J. Russian Phys. Chem. Soc.*, **44**, 469 (1912).

[109] DUPONT, *Compt. rend.*, **156**, 1623 (1913).

[110] MADINAVEITIA and BLANES, *Soc. Espan. Fis. Quim.*, **10**, 381 (1913), *C. A.*, **7**, 3500.

[111] WIELAND and WISHORT, *Berichte*, **47**, 2082 (1914).

[112] BRETEAU, *Div. méth. hydrog.*, Paris, 1911, p. 26.

the ring being attacked.   *Toluene,* dissolved in acetic acid and subjected to hydrogenation for 8 hours, is not affected.[113]

581. Rhodium Black.   Rhodium black is more active than ruthenium.   Under the conditions given above, *cinnamic acid* is transformed into *phenyl-propionic* in 3 hours and into *cyclohexyl-propionic* in 15 hours.   *Toluene* can be hydrogenated to *hexahydrotoluene* in 12 hours by 10 % of its weight of the black.[113]

582. Iridium Black.   This black prepared by reducing the *chloride* by sodium formate, has an activity entirely analogous to that of ruthenium black (580).[113]

583. Osmium Black.   This black, prepared by reducing osmic anhydride by formic acid, does not effect any hydrogenation of *cinnamic acid* in 5 hours.[113]

Osmium dioxide has been mentioned as able to hydrogenate oils when used to the amount of 0.5 %,[114] but it is certain that it acts after it is reduced to the metal which is the true catalyst.[115]

[113] Madinaveitia, *Soc. Espan. Fis. Quim.,* **11,** 328 (1913).

[114] Lehmann, *Arch. Pharm.,* **251,** 152 (1913), *C. A.,* **8,** 586 (1914).

[115] Norman and Schick, *Arch. Pharm.,* **252,** 208 (1914).

CHAPTER XII

HYDROGENATIONS (Continued)

DIRECT HYDROGENATION OF LIQUIDS IN CONTACT WITH METAL CATALYSTS (Continued)

III. METHOD OF IPATIEF

584. THIS method consists in warming the substance to be hydrogenated in contact with *nickel* or *nickel oxide* and hydrogen compressed to at least 100 atmospheres in a very strong container. The hydrogenation velocity is greater when the oxide is used, which Ipatief attributes to the real catalytic power of the oxide. As we have seen above (80), catalytic power appears to belong exclusively to the metal; since the temperature is always above 250°, the nickel oxide must at least in part be reduced to the metal which is more active than the metal prepared in advance and which has been subjected to incandescence more or less intense while being introduced into the container, being thereby agglomerated and reduced in catalytic power.

The nickel is frequently replaced by copper, copper oxide, iron or palladium, or even by zinc powder.

585. **Apparatus.** The apparatus used for all of this work consists of a soft steel tube lined with copper, holding 250 to 275 cc. and capable of sustaining 600 atmospheres at 600°.[1] It is heated electrically by a nickel resistance wire. Changes of pressure are shown by a manometer. If the apparatus has been filled with hydrogen at a certain pressure, the pressure increases according to the rise of temperature, if there is no absorption of hydrogen or evolution of gas, but less rapidly if there is absorption of hydrogen, while if there is decomposition with evolution of gas, the pressure increases more rapidly and this increase measures the rate of decomposition.

The material of which the apparatus is constructed appears to influence the results in some way. Thus in a bronze tube the use of reduced copper as catalyst did not effect the complete hydrogenation of the aromatic nucleus, while this was realized in an iron apparatus.[2]

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[1] IPATIEF, *Berichte*, **37**, 2961 (1904). — *J. Russian Phys. Chem. Soc.*, **36**, 786 (1904), *C.*, **1904** (2), 1020.

[2] IPATIEF, *J. Russian Phys. Chem. Soc.*, **42**, 1557 (1910).

Use of Nickel

In order to carry out a hydrogenation, about 25 g. of the material to be hydrogenated is placed in the apparatus with 2 to 3 g. nickel oxide (NiO or Ni_2O_3) and hydrogen is admitted to 100 atmospheres at which pressure it holds about one gram molecule of hydrogen. The temperature of heating may reach 400° or even 600° and the resulting pressure may be 2.5 or 3 times the original, i.e. 250 to 300 atmospheres. The necessity of having an expensive apparatus and the real dangers of its use are against the general employment of the method of Ipatief, which is not superior to the method of Sabatier and Senderens except in special cases where the slowness of hydrogenation or the need of high pressures requires its use. Most organic substances give the same products by both methods.

586. **Formation of Methane.** The direct hydrogenation of carbon in the presence of nickel, oxide of nickel, or nickel oxide and alumina, does not take place below 600° under moderate pressures of hydrogen, but under very high pressures, *methane* is produced above 500°, the amount increasing with rise of temperature.

The reduction of *carbon dioxide* to *methane* which takes place incompletely at 450° under ordinary pressure, is not more complete at high pressures even with an excess of hydrogen.[3]

587. **Ethylene Double Bonds.** The hydrogenation of substances containing ethylene bonds is readily effected.

Oleïc acid heated a long time at 100° with finely divided nickel and hydrogen at 25 atmospheres is not affected, but under 60 atmospheres pressure it is changed to *stearic acid* in 12 hours. *Liquid* fats are transformed to *solid*.[4]

50 g. *cottonseed oil* with 3 g. nickel oxide at 220–230° with hydrogen at 60 atmospheres gave in 4 hours a fat with iodine number (938) of only 11, while at ordinary pressures this result was obtained only at 255.°[5][6]

Dimethyl-allyl-carbinol is changed to *dimethyl-propyl-carbinol* under the same conditions.

At 140 to 150°, *mesityl oxide* gives *methyl-isobutyl-ketone* mixed with a little of the corresponding alcohol.

Cyclohexene is reduced to *cyclohexane*.

[3] IPATIEF, *J. prakt. Chem.* (2), **87**, 479 (1913).

[4] FOKIN, *J. Russian Phys. Chem. Soc.*, **38**, 419 and 855 (1906).

[5] IPATIEF, J. *Russian Phys. Chem. Soc.*, **46**, 302 (1914).

[6] With high speed stirring this reduction can be accomplished in about the same time with 0.1 g. nickel on infusorial earth with hydrogen at atmospheric pressure at 180°. — E. E. R.

588. Aldehydes and Ketones.   The transformation of aliphatic aldehydes and ketones into the alcohols can be accomplished, but it is limited by the inverse reaction of dehydrogenation especially when the temperature exceeds 200 to 250°.

Isobutyric and *isovaleric aldehydes* are partly reduced to the corresponding alcohols at 250° and 100 atmospheres.

At 250° *acetone* is completely changed to *isopropyl alcohol* and the same is true of various aliphatic ketones at around 200°. At about 280° the hydrogenation is limited by the inverse reaction which increases with elevation of temperature. From 300 to 325° acetone no longer gives any alcohol since isopropyl alcohol is decomposed into water, propane and lower saturated hydrocarbons, especially methane.[7]

Laevulose in solution is transformed, at 130° under 100 atmospheres, to α-*mannite*, *glucose* into *sorbite*, and *galactose* into *dulcite*.

589. Aromatic Nucleus.   The hydrogenation of the aromatic nucleus is realized in all cases.

Benzene is totally changed to *cyclohexane* in 1.5 hours at 250° with 8% nickel oxide. Nickel sesquioxide gives better results than the monoxide. At 300° the cyclohexane produced does not remain but is decomposed into benzene, methane and carbon.[8]

At 250° *diphenyl* is reduced to *dicyclohexyl* and *dibenzyl* to *dicyclohexylethane*.

At 245° *phenol* is transformed in 14 hours to *cyclohexanol* accompanied by some *cyclohexane*. At 200° *hydroquinone* gives *quinite*.[9] The product is a mixture of the *cis* and *trans* forms, but the yield is poor, as most of the diphenol goes into resinous products.[10]

At 230° under 100 atmospheres, *phenyl oxide* gives in 12 hours a mixture of *cyclohexyl oxide*, *cyclohexanol* and *cyclohexane*.[11]

Anisol, $C_6H_5OCH_3$, in 24 hours at 240° under 100 atmospheres, gives 40% *hexahydroanisol* accompanied by cyclohexanol and cyclohexane.

Guaiacol, $o.HO.C_6H_4.OCH_3$, in 12 to 15 hours at 220 to 240° and 100 atmospheres, yields *hexahydroguaiacol* with cyclohexanol and a little cyclohexane.[12]

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[7] IPATIEF, *J. Russian Phys. Chem. Soc.*, **38**, 75 (1906) and **39**, 681 (1907), *C. A.*, **1**, 2877. — *Berichte*, **40**, 1270 (1907).

[8] IPATIEF, *J. Russian Phys. Chem. Soc.*, **39**, 681–693 (1907), *C. A.*, **1**, 2877 and 2878.

[9] IPATIEF, *J. Russian Phys. Chem. Soc.*, **38**, 75 (1906) *C.*, **1906**, (2), 86. — *Berichte*, **40**, 1281 (1907).

[10] IPATIEF and LOUVOGOI, *J. Russian Phys. Chem. Soc.*, **46**, 470 (1914).

[11] IPATIEF and PHILIPOW, *J. Russian Phys. Chem. Soc.*, **40**, 501 (1908), *C.*, **1908** (2), 1098. — IPATIEF, *Berichte*, **41**, 993 (1908).

[12] IPATIEF and LOUVOGOI, *J. Russian Phys. Chem. Soc.*, **46**, 470 (1914).

590. The hydrogenation of phenols having unsaturated side chains is accomplished in two steps. At 95° and 30 to 50 atmospheres, only the side chain is attacked but by raising the temperature to 185 to 200°, the nucleus is also hydrogenated.

Thus, *anethol.* $p.CH_3O.C_6H_4.CH : CH.CH_3$, with 10 % nickel at 95° and 50 atmospheres is transformed completely in 4 hours to *methoxy-propyl-benzene*, but 20 hours at 200° produce *propyl-cyclohexane*, the methoxy group being reduced to water and methane.

Likewise *eugenol*, $H_3C(HO)C_6H_3.CH_2CH : CH_2$, and *isoeugenol*, $H_3C(HO)C_6H_3.CH : CH.CH_3$, furnish *methoxy-propyl-phenol* in 2 or 3 hours at 29°, while at 195° in 7 hours, the chief product is *methoxy-propyl-cyclohexane*, $H_3CO \cdot C_6H_{10} \cdot C_3H_7$, the phenol group being eliminated.

The *methyl ether* of *eugenol* adds only H_2 at 95°, but in 10 hours at 210°, the same product is obtained as from eugenol.

Safrol and *isosafrol* are not hydrogenated at ordinary pressure at 140 to 160° with constant agitation for 5 hours, but under 50 atmospheres at 93°, *dihydrosafrol*, boiling at 228°, is obtained in 2 hours. In 10 to 12 hours at 180°, a product is obtained boiling at 207° which appears to be *methoxy-propyl-cyclohexane.*[13]

By 50 hours heating at 220° under 115 atmospheres, *aniline* gives 40 to 50 % of *cyclohexyl-amine*, about 10 % *dicyclohexyl-amine* and some *cyclohexyl-aniline.*[14]

Diphenyl-amine yields *dicyclohexyl-amine.*[15]

Benzaldehyde, at 200°, gives *toluene* and *methyl-cyclohexane*,[16] while at 280° in 12 hours, toluene, dibenzyl and resinous products are obtained.[14]

Aromatïc ketones act as they do in Sabatier's process (389) and yield hydrocarbons, *benzophenone* going into *diphenyl-methane* and *benzoïne* into *dibenzyl.*[15] [17]

Ipatief's process is useful for the hydrogenation of aromatic acids, but it is not well to use the free acids which attack the nickel nor the esters which give poor results (*ethyl terephthalate* is decomposed into *ethyl p.toluate*, methane and carbon dioxide), but the alkaline salts. Thus *potassium benzoate* gives 40 % of the *hexahydrobenzoate* at 280° in 9 hours and *sodium benzoate* is even more readily hydrogenated.

[13] IPATIEF, *Berichte*, **46**, 3589 (1913).

[14] IPATIEF, *Berichte*, **41**, 993–1001 (1908).

[15] IPATIEF, *J. Russian Phys. Chem. Soc.* **40**, 491 (1908), *C.*, **1908** (2), 1098.

[16] IPATIEF, *J. Russian Phys. Chem. Soc.*, **38**, 75 (1906), *C.*, **1906** (2), 86.

[17] IPATIEF, *J. Russian Phys. Chem. Soc.*, **38**, 75 (1906) and **39**, 693 (1907), *C. A.*, **1**, 2877.

Potassium phthalate gives the *hexahydrophthalate* at 300° in good yield.[18]

Sodium cinnamate gives the *cyclohexyl-propionate* at 300° under 100 atmospheres.[19]

591. Terpenes. Terpene compounds undergo the regular transformations.[20]

Limonene is transformed into dihydrolimonene and then into *menthane* at 300–320° under 120 atmospheres.

At 265° *pinene* gives *pinane* and *menthane* at 300°.

At 240°, in 10 to 15 hours, *camphene* furnishes an *isocamphane* melting at 57° and boiling at 162.5°.

At 280°, under 120–130 atmospheres, *carvone* passes into *carvomenthone*. At 220°, *pulegone* gives *menthone*, which at 280° is mixed with menthane.

Camphor is completely changed into *borneol* at 350°.

592. Various Rings. At 250° under 120 atmospheres, *naphthalene* gives, in turn, *tetrahydro-* and *decahydro-naphthalene*.

The α- and β-*naphthols* are changed to α- and β-*decahydronaphthols*, melting at 57° and 99° respectively.[21]

Anthracene, submitted to repeated hydrogenations at 260–270° under 100 to 125 atmospheres for 10 to 16 hours, gives in succession, *tetrahydro-*, *decahydro-* (m.73°) and finally *perhydroanthracene* (m.88°) and at the same time is partially destroyed.

At 400°, *phenanthrene* gives better results, the *dihydro-* and then the *tetrahydro-* being obtained and, by a second operation, the *octahydro-* and *perhydrophenanthrene* with the odor of caoutchouc.[22]

Quinoline first yields *tetrahydroquinoline* and then, almost quantitatively, *decahydroquinoline*.[23]

Use of Iron

593. At 350–400°, *iron* transforms aliphatic aldehydes and ketones into the alcohols. *Acetone*, at 400° and 103 atmospheres in 20 hours yields 25 % of isopropyl alcohol. *Isobutyric aldehyde* gives 75 % of the corresponding alcohol at 350°, but *acetaldehyde* is partly resinified and partly decomposed into carbon monoxide and methane.

[18] IPATIEF and PHILIPOW, *J. Russian Phys. Chem. Soc.*, **40**, 501 (1908), *C.*, **1908** (2), 1098. — IPATIEF, *Berichte*, **41**, 993 (1908).

[19] IPATIEF, *J. Russian Phys. Chem. Soc.*, **41**, 1414 (1909).

[20] IPATIEF, *Berichte*, **43**, 3546 (1910). — IPATIEF and MATOW, *Berichte*, **45**, 3205 (1912).

[21] IPATIEF, *J. Russian Phys. Chem. Soc.*, **39**, 693 (1907), *C. A.*, **1**, 2877. — *Berichte*, **40**, 1281 (1907).

[22] IPATIEF, JAKOWLEW and RAKITIN, *Berichte*, **41**, 996 (1908).

[23] IPATIEF, *J. Russian Phys. Chem. Soc.*, **40**, 491 (1908), *C.*, **1908** (2), 1098.

The hydrogenation of the aromatic nucleus does not take place, even at 420°, but *cyclohexane* is brought back to benzene.[24]   At 280° *benzaldehyde* gives a mixture of *toluene* and *dibenzyl*. The same result is obtained when *benzyl alcohol* is hydrogenated at 350° and 96 atmospheres.[25]

Use of Copper

594. Copper, or copper oxide (certainly reduced to the metal), readily permits the hydrogenation of ethylene *bonds* at 300 to 350° under 100 to 200 atmospheres, but when used alone does not effect the hydrogenation of the benzene ring.[26]

Sodium cinnamate is changed to the *phenyl-propionate*.[27]

Unsaturated side chains of phenols are saturated at 270 to 300° without modification of the nucleus.[28]

Acetone yields 65 % of *isopropyl alcohol* at 280–300°.

Pinene is transformed to *pinane*, while *camphene* gives two hydrides, a solid melting at 66° and a liquid boiling at 162°.[29]

The sodium salts of the two *naphthalic* acids act differently when hydrogenated with copper at 300° under 100 atmospheres. The α acid furnishes *tetrahydronaphthalene* directly, while the β leads first to the *tetrahydro-naphthalic* acid and then to *decahydronaphthalene*.[27]

Use of Other Metals

595. **Zinc powder** can cause the reduction of acetone to the alcohol with a yield of 50 %.

By using *palladium*, reduced from the chloride by formates, in the proportion of 1 g. to 30 g. of the substance to be hydrogenated under 110 atmospheres at 110°, *methyl-ethyl-acroleïne*, $C_2H_5.CH : CH(CH_3)-$ $\cdot CHO$, is transformed in 2 or 3 days to *methyl-pentanol*.

Mesityl oxide is changed in 2 days at 110° to *methyl-isobutyl-ketone*.

By continuous shaking at 110°, *citral* is reduced to the *decanol* with a little of the *decane*. The same may be said of *geraniol*.

Acetyl-acetone, under 116 atmospheres at 109° is changed to *pentanediol* in six hours.

Carbohydrates dissolved in aqueous alcohol are changed to the

[24] IPATIEF, *J. Russian Phys. Chem. Soc.*, **38**, 75 (1906) and **39**, 681 (1907), *C. A.*, **1**, 2877.

[25] IPATIEF, *J. Russian Phys. Chem. Soc.*, **40**, 489 (1908), *C.*, **1908** (2), 1098.

[26] IPATIEF, *Berichte*, **43**, 3387 (1910).

[27] IPATIEF, *J. Russian Phys. Chem. Soc.*, **41**, 1414 (1909).

[28] IPATIEF, *Berichte*, **46**, 3589 (1913).

[29] IPATIEF and DRACHUSSOF, *J. Russian Phys. Chem. Soc.*, **42**, 1563 (1911), *C.*, **1911** (1), 1292.

corresponding hexites at 110° under 100 atmospheres. *Laevulose* yields *mannite*, *glucose* goes into *sorbite* and *galactose* into *dulcite*.[30]

IV. HYDROGENATIONS BY NICKEL IN LIQUID SYSTEMS UNDER LOW PRESSURES

596. Very extensive use has been made of the common metals, particularly *nickel*, for hydrogenation in liquid medium in the case of liquid fats the molecules of which contain ethylene bonds. The description of the methods followed and the results obtained is the special object of the last chapter but the same process can be generalized and extended to a large number of cases. The fundamental condition of success is a sufficiently energetic agitation in the hydrogen. A pressure of several atmospheres is useful but not indispensable, the hydrogenation being capable of being carried out with even reduced pressure. Simply bubbling the hydrogen through the liquid is not sufficient.

Brochet has tried to define exactly the conditions for using this method.[31]

597. **Apparatus.**   Different forms of apparatus may be used according to the amount of the work to be done and the magnitude of the pressure to be used. The pressures run from 1 to 50 atmospheres, being usually around 10 to 15.

A red copper autoclave of 1200 cc. capacity, which can operate satisfactorily with 700 to 800 cc. of liquid, may be used. The bronze cover is fitted accurately and made tight with lead foil packing, being held in place by screw clamps. It is fitted with a thermometer-well dipping into the liquid, a pressure gauge, and a valve for the introduction of the hydrogen. The apparatus is heated electrically by a ferro-nickel coil insulated by asbestos and surrounded by sheet asbestos to keep the heat in. After the introduction of the liquid to be hydrogenated, either alone or in solution, and the addition of the catalyst, the autoclave is closed and connected with the hydrogen tank which is placed along side on the platform of a mechanical shaker. When the operation is finished, the catalyst is filtered off and may frequently be used immediately for another hydrogenation.[32]

Brochet uses a 500 cc. glass cylinder connected with a hydrogen tank by means of a bubble counter which measures the amount of hydrogen absorbed, and enables one to follow the course of the reaction.

[30] IPATIEF, *J. Russian Phys. Chem. Soc.*, **44**, 1002, and 1710 (1912); *C. A.*, **7**, 1171, and *Berichte*, **45**, 3218 (1913).

[31] BROCHET, *Bull. Soc. Chim.* (4), **13**, 197 (1913) and **15**, 554 (1914).

[32] A convenient laboratory apparatus with high speed stirring has been described by REID, *J. Amer. Chem. Soc.*, **37**, 2112 (1915). — E. E. R.

598. **Catalysts.** The nickel used is prepared by reducing at about 300° the oxide prepared by calcining the carbonate, nitrate or oxalate. After cooling in a current of hydrogen, the reduced metal is plunged quickly into the liquid to be hydrogenated, avoiding contact with the air as much as possible.

The nickel may be used alone as a metal powder or incorporated with inert materials such as infusorial earth, pumice, or charcoal (126). This incorporation with a carrier is advantageous and gives, on reduction at 450°, a catalyst which is more active than the metal alone reduced at 350°, and *a fortiori* more active than the metal alone reduced at 450°.[33]

Nickel on a carrier is much less sensitive to toxic agents than nickel alone. Thus for the metal alone, the amount of hydrogen sulphide required to kill the catalyst is 0.02–0.005 g. to 0.5 g. of the catalyst, according to the method of preparation, but may be as high as 0.1 g. for the metal on a porous support.[34]

We have seen (584) that Ipatief has found it advantageous with his method to use an oxide of nickel, such as NiO or Ni_2O_3, in place of the metal, and that he considers the oxide more active. The same substitution has been proposed for the hydrogenation of oils (943), in which the oxides should show a greater activity and should be less susceptible to the action of poisons, particularly sulphur.[35] But in all cases the activity of the oxide may be explained by assuming that it is partially reduced to the metallic state, the metal being more active on account of being formed within the liquid and in a better state of subdivision. This is the opinion of Brochet, who considers the presence of the free metal necessary for hydrogenation but thinks that it is activated by the presence of foreign substances, such as its oxide, or salts or even other metals.[36]

The presence of metallic nickel in the oxide which is used as catalyst has been denied by Erdmann, who bases his conclusion on the absence of conductivity in the catalyst after it has been freed from fatty material.

At any rate, it is well established that at the temperature at which the hydrogenation of oils is carried on, nickel oxide is reduced to the suboxide, Ni_4O, which is *necessarily* slowly reduced at these same temperatures to the free metal, the presence of which is easily shown by the direct formation of nickel carbonyl by the action of carbon

[33] KELBER, *Berichte*, **49**, 55, (1916).
[34] KELBER, *Berichte*, **49**, 1868 (1916).
[35] BEDFORD and ERDMANN, *J. prakt. Chem.* (2), **87**, 425 (1913).
[36] BROCHET, *Bull. Soc. Chim.* (4), **15**, 770 (1914).

monoxide below 100°.[37] Meigen and Bartels,[38] Norman and Pungs,[39] and later Frerichs, who found an appreciable conductivity in the oxide which had served for the hydrogenation of oil,[40] have come to the same conclusion, that is, that the oxide is inactive in hydrogenation, the activity belonging only to the free metal.

Erdmann has claimed that the most active factor in hydrogenation is a suboxide, such as Ni_2O, which would form an unstable hydride with hydrogen, e.g. $O\begin{smallmatrix}\diagup NiH \\ \diagdown NiH\end{smallmatrix}$, which is capable of transferring hydrogen to the molecules which can take it up. This special aptitude of the suboxide has been claimed by Senderens and Aboulenc, according to whom acetone can be hydrogenated at 110° under 30 atmospheres pressure by the suboxide but not by the metal.[41]

The amount of catalyst may be as low as 0.5 % of the liquid to be hydrogenated, but it is better to use larger amounts in order to hasten the reaction.[42]

599. Method of Work. It is best to operate at least 20° below the boiling point of the liquid used as solvent so that its vapor will not dilute the hydrogen too much. If substances are hydrogenated without solvent, 100 to 150° is the usual range of temperatures but sometimes from 150 to 200°.

Alcohol, more or less diluted, and acetic acid are the most favorable solvents. Benzene, acetone, ether, and ethyl acetate are not so good, while chloroform is rather harmful.[43]

The course of the reaction is easily followed, either by the pressure gauge or by the bubble counter, which shows directly the volume absorbed. This enables one to see at what temperature the reaction goes best.

600. Results Obtained. *Nitro* derivatives are readily changed to the corresponding *amines*. *Azo* and *hydroazo* compounds are split into two amines; but by operating in the presence of caustic soda which moderates the action of the catalyst, it is possible to obtain *azoxy, azo, hydrazo* and finally *amino* from *aromatic nitro* compounds.[44]

[37] Sabatier and Espil, *Compt. rend.*, **158**, 674 (1914).

[38] Meigen and Bartels, *J. prakt. Chem.* (2), **89**, 296 (1914).

[39] Norman and Pungs, *Chem. Zeit.*, **39**, 29 (1915), *C. A.*, **9**, 1552.

[40] Frerichs, *Arch. Pharm.*, **253**, 512 (1915).

[41] Senderens and Aboulenc, *Bull. Soc. Chim.* (4), **17**, 14 (1915).

[42] In hydrogenating cotton seed oil, 0.1 % nickel on a carrier is ample and even 0.01 % gives fair results. — E. E. R.

[43] Kelber, *Berichte*, **49**, 55 (1916).

[44] Brochet, *Bull. Soc. Chim.* (4), **15**, 554 (1914).

601. **Ethylene Double Bonds.**   These are easily saturated at low temperatures, even in the cold, with the evolution of heat.

A mixture of *ethylene*, with hydrogen in excess, is changed to *ethane* by being passed at atmospheric pressure through a saturated hydrocarbon in which a nickel catalyst is kept in suspension by rapid stirring.[45]

α-Octene, treated in alcohol solution with 20 % of active nickel and hydrogen at 15 atmospheres, is completely changed to *octane* in the cold.   This can be accomplished under atmospheric pressure but takes much longer.[46]

Oleïc acid is reduced to *stearic acid* at 250° with a velocity which is nearly proportional to the pressure of the hydrogen.[47]

The aliphatic esters of *oleïc acid* are transformed into stearic esters.

The salt formed by combining hot oleïc acid with *aniline* is rapidly hydrogenated to a brittle solid melting at 76°.[48]

Cinnamic acid, in twice its weight of amyl alcohol, is completely changed to *phenylpropionic* in 45 minutes by 10 % of nickel at 100° under 15 atmospheres.   The fact that the acid attacks the nickel does not hinder the reaction.   However, it is better to use *sodium cinnamate* in 4 parts of water, which is hydrogenated in the cold.

Methyl cinnamate, dissolved in methyl alcohol, is changed to *methyl phenylpropionate*[49] in the cold in 3 hours under 15 atmospheres pressure.   Under ordinary pressure the action is much slower, the reduction of *ethyl cinnamate* requiring 7 hours at 70°.[50]

Anethol, $CH_3O.C_6H_4.CH:CH.CH_3$, is rapidly transformed into *methoxy-propyl-benzene* when treated without solvent with 10 % of nickel at 60–80° under 15 atmospheres, but requires 5 times as long at 1 atmosphere.

Isosafrol, dissolved in 3 parts of alcohol with 19 % of nickel, adds H_2 in an hour at 65°.

Geraniol and *linalool* saturate their double bonds, but *allyl alcohol* does not at 70° under 15 atmospheres, neither does *allyl sulphocyanate*. *Piperonyl-acrilic* acid gives *piperonyl-propionic* acid in the cold under 15 atmospheres.[51]

The *acetylene triple bond* is also saturated without difficulty.

[45] RATHER and REID, *J. Amer. Chem. Soc.*, **37**, 2115 (1915).

[46] BROCHET and BAUER, *Bull. Soc. Chim.* (4), **17**, 50 (1915), and *Compt. rend.*, **159**, 190 (1914).

[47] SHAW, *J. Soc. Chem. Ind.*, **33**, 771 (1914).

[48] ELLIS and RABINOVITZ, *J. Ind. Eng. Chem.*, 8, 1105 (1916).

[49] BROCHET and BAUER, *Loc. cit.*

[50] BROCHET and CABARET, *Compt. rend.*, **159**, 326 (1914).

[51] BROCHET and BAUER, *Bull. Soc. Chim.* (4), **17**, 50 (1915).

602. *Aldehydes* and *ketones.*   Aldehydes and ketones are not appreciably hydrogenated under atmospheric pressure.   Thus the *allyl-ketones* dissolved in 5 parts of alcohol and treated at 60° with hydrogen under atmospheric pressure are hydrogenated in several hours to the *saturated ketones* without affecting the ketone group.[52]

On the contrary, by working under pressure it is possible to change aldehydes and ketones to the corresponding alcohols.[53]

603. Various Rings.   The hydrogenation of the *benzene ring* or of similar rings is much more difficult to attain and is scarcely realizable except in the case of *phenols* and of compounds directly related to them.[54]

With ordinary *phenol* the addition of hydrogen takes place slowly from 50° up and rapidly between 100 and 150° under 15 atmospheres, with complete transformation into *cyclohexanol* without the simultaneous production of *cyclohexanone.*

Likewise several hours are sufficient for the hydrogenation of α- and β-*naphthols* at 150° under 15 atmospheres.

Eugenol, $CH_3O(OH)C_6H_3.CH_2.CH:CH_2$, adds H_2 rapidly at 60° and 15 atmospheres to form *propyl-methoxy-phenol* but the ring is not hydrogenated unless the operation is carried on at 150°.

Indigotine.   Indigo, dry or in paste, suspended in water containing a little caustic soda (10 g. indigo to 250 c. dilute caustic soda) is reduced at 70° by 5 g. nickel to *indigo white* in 40 minutes.   The same reaction applies to *thio-indigo* and to *malachite* green which is reduced to the leuco base.[55]

Hydrogenations by nascent Hydrogen in Liquid Systems in contact with Metals

604. The decomposition of *formic acid* by the catalytic action of metals of the platinum group provides hydrogen (824) which can be used in the liquid itself to effect hydrogenations.   By the use of spongy or *colloidal palladium*, *cinnamic* acid can be transformed into *phenylacetic* or *quinine* into *hydroquinine.*[56]

[52] CORNUBERT, *Compt. rend.*, **159,** 78 (1914).

[53] BROCHET and CABARET, *Compt. rend.*, **159,** 326 (1914).

[54] The hydrogenation of naphthalene is thoroughly described by SHROETER, *Annalen*, **426,** 1, (1922). — E. E. R.

[55] BROCHET, *Compt. rend.*, **160,** 306 (1915).

[56] VEREIN. CHININFABR. ZIMMER & Co., *German patent*, 267,306, 1914, *C.*, **1914** (1), 88.

CHAPTER XIII

VARIOUS ELIMINATIONS

§ I. — ELIMINATION OF HALOGENS

605. THE classical method for the elimination of halogens from chlorine, bromine or iodine compounds is treatment with sodium.[1] The presence of *benzene* or *petroleum ether* retards this reaction greatly, but ordinary ether and ethyl acetate usually accelerate it.[2] The use of small amounts of *acetonitrile* greatly facilitates the reaction. Thus sodium does not act on *methyl iodide* in the cold but the addition of one or two drops of acetonitrile causes an immediate and abundant evolution of *ethane*, $CH_3.CH_3$.

The same is true with *ethyl, propyl, isopropyl* and *allyl iodides, trimethylene bromide* and *benzyl chloride*. *Ethyl cyanide* produces a similar catalytic effect and *propyl cyanide* is less effective while *benzonitrile* and *benzyl cyanide* have no such effect.[3]

§ 2. — ELIMINATION OF NITROGEN

606. **Diazo Compounds.** In many important reactions of aromatic diazo compounds, a molecule of nitrogen is eliminated. *Cuprous salts* are frequently useful or indispensable catalysts for these decompositions. *Copper powder* can produce the same effects, doubtless through the initial formation of cuprous compounds.

Diazobenzene hydroxide, $C_6H_5.N : N.OH$ decomposes immediately even at 0° in the presence of copper powder to form phenol and nitrogen. The copper for this purpose is precipitated by zinc dust in a saturated solution of copper sulphate, washed with water and then with a very dilute solution of hydrochloric acid and preserved wet and protected from the air.[4]

607. **Hydrochloric acid** reacts with diazo chlorides, on boiling, to give the corresponding aromatic chloride, on condition that the de-

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[1] WURTZ, *Ann. Chim. Phys.* (3), **44**, 275 (1855).
[2] ELBS, *Synth. Darstel. d. Kohlenst., Leipzig*, 1889, **2**, 59.
[3] MICHAEL, *Amer. Chem. Jour.*, **25**, 419 (1901).
[4] GATTERMANN, *Berichte*, **23**, 1220 (1890).

composition takes place in the presence of *copper powder* or *cuprous chloride*.[5] We have:

$$C_6H_5.N_2.Cl + HCl = N_2 + C_6H_5.Cl + HCl.$$
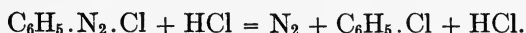
The cuprous chloride is used in hydrochloric acid solution.

This action of cuprous chloride has been explained by assuming that it acts in the presence of hydrochloric acid as a reducing agent giving cupric chloride and hydrogen:

$$2CuCl + 2HCl = 2CuCl_2 + 2H$$

and $$2H + C_6H_5.N : NCl = C_6H_5.NH.NHCl.$$
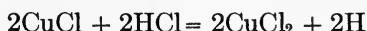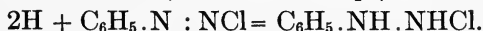
The hydrazine compound thus formed reduces the cupric chloride:

$$2CuCl_2 + C_6H_5.NH.NHCl = \underset{\text{regenerated}}{\underline{2CuCl + 2HCl}} + C_6H_5.Cl + N_2.$$
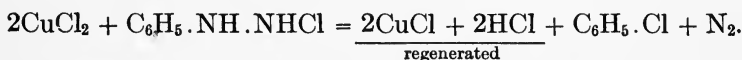
The regenerated cuprous chloride repeats the same effects.

608. Hydrobromic acid reacts in a similar way on diazonium bromides in the presence of *cuprous bromide*. The cuprous bromide is prepared by warming 20 g. copper turnings with a solution of 12.5 g. copper sulphate and 36 g. potassium bromide in 80 cc. water containing 11 g. sulphuric acid.[6]

609. Diazonium salts in water solution with sodium nitrite, in the presence of copper powder or moist cuprous oxide, are transformed into *nitro* compounds (Sandmeyer reaction):

$$C_6H_5.N_2.Cl + NaNO_2 = C_6H_5.NO_2 + NaCl + N_2.$$
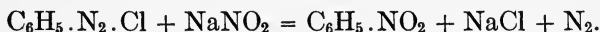
610. Diazonium salts yield the corresponding *aromatic isocyanates*, $C_6H_5.NCO$, when treated with *potassium isocyanate* in presence of *copper powder*.[7]

611. Hydrazine Compounds. *Phenylhydrazine* is decomposed at 150° into aniline, nitrogen and ammonia, on contact with cuprous chloride, bromide, or iodide:

$$3C_6H_5.NH.NH_2 = 3C_6H_5.NH_2 + N_2 + NH_3.$$

The chloride acts more rapidly than the bromide and this more rapidly than the iodide. When more than 1% of the chloride is added, the decomposition is violent and almost explosive. The crystallized compound, $CuI.2C_6H_5.NH.NH_2$, which may serve as an intermediate step in the catalysis, has been isolated.[8]

[5] Sandmeyer, *Berichte*, **17**, 1635 (1884).

[6] Sandmeyer, *Berichte*, **17**, 2652 (1884).

[7] Gattermann, *Berichte*, **23**, 1220 (1890).

[8] Arbusow and Tichwinsky, *Berichte*, **43**, 2295 (1910) and *J. Russian Phys. Chem. Soc.*, **45**, 69 (1913), *C. A.*, **7**, 2225.

The *hydrazones* derived from hydrazine and saturated cyclic ketones are decomposed, with the evolution of nitrogen, on contact with a small fragment of solid *potash.*

Cyclohexone hydrazone gives cyclohexane in a violent reaction:

$$CH_2 \diagup \substack{CH_2.CH_2 \\ CH_2.CH_2} \diagdown C:N.NH_2 = CH_2 \diagup \substack{CH_2.CH_2 \\ CH_2.CH_2} \diagdown CH_2 + N_2.$$
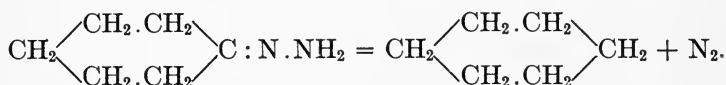
In every case the hydrocarbon obtained contains CH_2 in place of the CO of the *ketone.* Thus hydrazones from the *methyl cyclohexones* yield *methyl cyclohexane,* that from *camphor* furnishes *camphane,* $C_{10}H_{18}$ melting at 158°, and that from *fenchone* leads to *fenchane,* boiling at 151°.[9]

612. 3, 5. — **Diphenyl-pyrazoline** heated with fragments of potash and *platinized* porous porcelain decomposes into nitrogen and *diphenylcyclopropane.*[10]

$$C_6H_5.CH \diagup \substack{-CH_2- \\ NH.N} \diagdown C.C_6H_5 \rightarrow C_6H_5.CH \diagup \substack{CH_2} \diagdown CH.C_6H_5 + N_2.$$
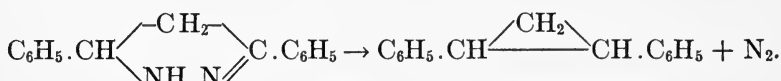
§ 3. — SEPARATION OF FREE CARBON

613. In many cases the dehydrogenation of hydrocarbons leads to the separation of free carbon and we shall see (Chapter XXI) that various finely divided metals frequently provoke this decomposition. But it is well to consider here a very important reaction which takes place with the separation of carbon from carbon monoxide in contact with certain substances.

614. Decarbonization of Carbon Monoxide. In the reduction of the oxides of iron, nickel and cobalt carried on above 400° by carbon monoxide, it has long been known that carbon is deposited and this continues at the expense of the carbon monoxide according to the equation:

$$2CO = CO_2 + C.$$

Mond found that nickel can produce this effect between 350 and 450°.[11]

Sabatier and Senderens have shown that the reaction takes place with *reduced nickel* above 230°, elevation of temperature accelerating the decomposition of the carbon monoxide. With a layer of nickel

[9] KIZHNER, *J. Russian Phys. Chem. Soc.,* **43**, 582 (1911), *C. A.,* **6**, 347.

[10] KIZHNER, *J. Russian Phys. Chem. Soc.,* **47**, 1102 (1915), *C. A.,* **9**, 3051.

[11] MOND, LANGER and QUINCKE, *Chem. News,* **62**, 95 (1890).

35 cm. in length and a flow of gas of 25 cc. per minute, the amounts of carbon dioxide formed from 100 cc. of the monoxide were:

At 238° .... 1.2 cc.
    250° 3.8
    275° 17.9
    285° 23.2
    300° 40.5
    320° 49.0
    349° and above....... 50.0, complete transformation.

The reaction may be complete as can be shown by experiment; and besides, the inverse formation of carbon monoxide from carbon and the dioxide does not begin below 400°. We do not have to any extent:

$$C + CO_2 = 2CO,$$
nor: $$Ni + CO_2 = NiO + CO.$$
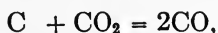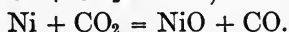
This would take place no more at higher temperatures, such as 650° and 800°.[12]

615. Reduced cobalt gives rise to the identical reaction at above 300°.

Finely divided iron, kept at 445° with carbon monoxide for several hours, transforms it completely into carbon dioxide with the deposition of carbon.[13]

Finely divided *platinum,* reduced *copper,* and finely divided *silver,* do not produce a similar effect on carbon monoxide below 450°.

616. The separation of carbon can be explained by assuming the temporary formation of *nickel* or *cobalt carbonyl* which the high temperature decomposes into metal, carbon, and carbon dioxide.[14]

But we can explain the phenomenon equally well by the mechanism which is apparent in the case of iron. At low temperatures, iron tends to reduce carbon monoxide to carbon with the formation of ferrous oxide:

$$Fe + CO = FeO + C,$$
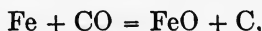
but at a higher temperature, there is the formation of carbon dioxide and iron:

$$FeO + CO = CO_2 + Fe.$$
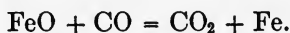
The iron thus regenerated can repeat the first reaction. These two successive steps may take place likewise with nickel and cobalt without our being able to perceive the intermediate compound, the oxide, since

[12] SABATIER and SENDERENS, *Bull. Soc. Chim.* (3), **29,** 294 (1903).
[13] BOUDOUARD, *Ann. Chim. Phys.* (7), **24,** 5 (1901).
[14] BERTHELOT, *Ann. Chim. Phys.* (6), **26,** 560 (1892).

the reduction of the oxide by the carbon monoxide takes place at a temperature lower than that at which the metal reduces the gas, the oxide of the metal can remain only in inappreciable amount. From this it can be seen that the reaction will take place better with nickel than with iron, since a considerable proportion of the iron is actually transformed into the oxide.[15]

617. **Manganous oxide,** which dehydrogenates alcohols after the manner of metals (701), appears to give, doubtless by a mechanism analogous to that which has just been described, a certain amount of decomposition of carbon monoxide into carbon and carbon dioxide, but it is always small below 350°.[16]

§ 4. — ELIMINATION OF CARBON MONOXIDE

618. The decomposition of *aldehydes* and *ketones* can take place as a consequence of the elimination of *carbon monoxide* under the influence of catalysts, either finely divided metals or anhydrous oxides acting at higher temperatures.

With *aldehydes* the reaction goes more readily and yields chiefly:

$$R.CO.H = CO + \underset{\text{hydrocarbon}}{RH.}$$

619. **Reduced nickel** acts energetically above 200°. The vapors of *propionic aldehyde* are rapidly dissociated at 235° into carbon monoxide and ethane. *Benzaldehyde* is largely decomposed at 220° into benzene and pure carbon monoxide.[17]

Furfural is changed by nickel at 270° into *furfurane*[18]:

$$\begin{array}{c} CH:CH \\ \cdot \qquad\quad >O \\ CH:C—CHO \end{array} \rightarrow \begin{array}{c} CH:CH \\ \cdot \qquad\quad >O. \\ CH:CH \end{array}$$
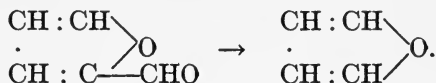
620. With *ketones* the result is more difficult to obtain. Starting with a ketone R.CO.R′ a certain amount of the hydrocarbon R.R′ may be formed but the débris resulting from the groups R and R′ are the chief products.

Acetone is decomposed by nickel, slowly at 240° and rapidly at 270°, yielding carbon monoxide and the CH_3 radicals which give a little ethane and ethylene but chiefly methane, hydrogen and *carbon*.[17]

621. **Reduced copper** has less effect: at 310° its action on *propionic aldehyde* is negligible and it is only at 350° or better at 400° that

[15] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 485 (1905).

[16] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20,** 315 (1910).

[17] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 474 (1905).

[18] PADOA and PONTI, *Lincei,* **15** (2), 610 (1906), *C.,* **1907** (1), 570.

carbon monoxide and a mixture of ethane, hydrogen and *butane* is obtained.[17]   Its action is energetic on *formaldehyde* which it decomposes almost completely into carbon monoxide and hydrogen.[19]   The resulting carbon monoxide can be absorbed by caustic soda present in the mixture and furnish, according to a well known reaction, *sodium formate.*[20]

Copper has no appreciable effect on ketones below 400°.

622. **Platinum sponge** and particularly *platinum black* have an intense destructive action on aldehydes.   *Propionic aldehyde* is attacked at 225°, and at 275° decomposes rapidly into the same gaseous products as are obtained with copper.[21]

The action on ketones is less intense.

623.   At 300° *palladium black* decomposes *formaldehyde* completely into carbon monoxide and hydrogen with traces of carbon dioxide and methane.   Likewise *acetaldehyde, propionic aldehyde, butyric aldehyde, benzaldehyde,* and the *toluic aldehydes* are more or less split at temperatures around 300° into carbon monoxide and the corresponding hydrocarbons.[22]

624.   The decomposition of *formic acid* into carbon monoxide and water which is effected by certain oxides, *titania, blue oxide* of *tungsten, alumina, silica,* and *zirconia,* and which can be regarded as an elimination of carbon monoxide, will be studied later (825), as also the decomposition of formic esters, which is chiefly according to this reaction (866):

$$H.CO_2C_nH_{2n+1} = CO + \underset{\text{alcohol}}{\underline{C_nH_{2n+1}.OH}}.$$
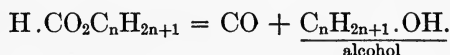
625.   Anhydrous *aluminum chloride* can decompose acid chlorides with the elimination of carbon monoxide.   This takes place with *dichloracetyl chloride* which is split into carbon monoxide and chloroform with *heptachlorpropane* as a by-product, resulting from the action of the chloroform on the original product.[23]

§ 5. — ELIMINATION OF HYDROGEN SULPHIDE

626. **Mercaptans.**   *Cadmium sulphide* catalyzes the decomposition of *mercaptans* according to two consecutive reactions exactly analogous to those according to which a primary alcohol is dehydrated to an ether and then to an unsaturated hydrocarbon (701).

[19] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **20**, 345 (1910).
[20] Loew, *Berichte*, **20**, 145 (1887).
[21] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4**, 475 (1905).
[22] Kuznezov, *J. Russian Phys. Chem. Soc.*, **45**, 557 (1913).
[23] Prins, *J. prakt. Chem.* (2), **89**, 414 (1914).

At a moderate temperature, we have:

$$2C_nH_{2n+1}.SH = H_2S + \underbrace{(C_nH_{2n+1})_2S.}_{\text{sulphide}}$$
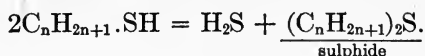
At a higher temperature, a more rapid decomposition yields hydrogen sulphide and the ethylene hydrocarbon:

$$C_nH_{2n+1}.SH = H_2S + C_nH_{2n}.$$
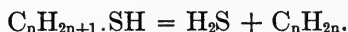
Thus *ethyl mercaptan*, $C_2H_5.SH$, passed over cadmium sulphide at 320°, is almost completely transformed into the neutral sulphide, $(C_2H_5)_2S$, while at 380° it is completely decomposed into hydrogen sulphide and ethylene.

Isoamyl mercaptan is changed into *isoamyl sulphide* at 360°, but above 400° gives hardly anything but amylene.

The decomposition of *primary aliphatic mercaptans* over cadmium sulphide at regulated temperatures constitutes a regular method of preparing primary sulphides from the mercaptans.

627. The mechanism of the decomposition is altogether analogous to that of alcohols (169). We can assume the formation of a cadmium *mercaptide* from the mercaptan and cadmium sulphide. This would decompose, according to the temperature, either into the neutral sulphide or into the ethylene hydrocarbon with the regeneration of the metal sulphide which would then repeat the reaction, thus playing the part of a catalyst.

We have at first:

$$CdS + 2C_nH_{2n+1}.SH = \underbrace{(C_nH_{2n+1}S)_2Cd}_{\text{mercaptide}} + H_2S$$

then:

$$(C_nH_{2n+1}S)_2Cd = CdS + \underbrace{(C_nH_{2n+1})_2S}_{\text{sulphide}}$$

and at a higher temperature:

$$(C_nH_{2n+1}S)_2Cd = CdS + H_2S + 2C_nH_{2n}.$$
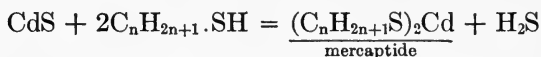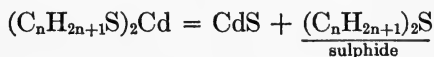
The transitory formation of the cadmium mercaptide is further indicated by the change of color of the sulphide, which takes on an orange tint quite different from the bright yellow of the original sulphide and retains that color after cooling in consequence of the persistence of a certain amount of the mercaptide.

628. **Secondary mercaptans** have a stronger tendency to decompose into the ethylene hydrocarbons but can, nevertheless, furnish some neutral sulphide.

Cyclohexyl mercaptan, passed over cadmium sulphide at 300°, gives

12 to 15 % of the sulphide but the major portion is decomposed to cyclohexene, while at 350° all of it goes into cyclohexene.[24]

629. Thiophenols. *Aluminum chloride* acts on a warm solution of *thiophenol* in petroleum ether, eliminating hydrogen sulphide and forming the diphenyl sulphide. At the same time some thianthrene,

$$C_6H_4 \diagdown{\!\!\!\!\!\!\!}^{S}_{S}{\!\!\!\!\!\!\!}\diagup C_6H_4,$$ is formed by loss of hydrogen.[25]
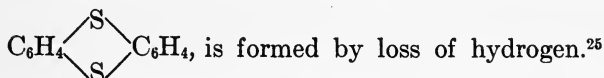
630. Formation of Thioureas. The *thioureas* can be obtained by the reaction of primary aromatic amines on carbon disulphide in the presence of a little *sulphur* as catalyst.

Thus 1 part each of aniline, alcohol, and carbon disulphide and 0.005 part crystallized sulphur are warmed for several hours on the steam bath to obtain symmetrical diphenyl-thiourea:

$$CS_2 + 2C_6H_5NH_2 = H_2S + CS\diagup^{NH.C_6H_5}_{\diagdown NH.C_6H_5}.$$
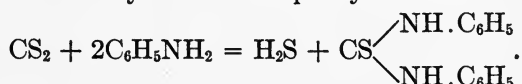
The *ortho* and *para toluidines*, the *naphthyl-amines* and even *p.aminophenol* give the same reaction.[26]

§ 6. — ELIMINATION OF AMMONIA

631. Reduced nickel has various effects on primary, secondary, and tertiary *amines*, and among these effects one is the elimination of ammonia.[27]

Above 300° this is a clean cut reaction with aliphatic amines containing less than 5 carbon atoms. Thus *ethylamine* splits up into ammonia and *ethylene*, which at that temperature is in turn decomposed into carbon, methane, hydrogen and ethane (910). We have:

$$C_2H_5.NH_2 = NH_3 + C_2H_4.$$
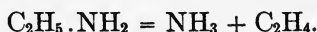
Amines containing five or more carbon atoms, e.g. *amyl-amine*, undergo this reaction and are simultaneously dehydrogenated to nitriles. This is true for *benzyl-amine* also.[28]

Aromatic amines, aniline and the toluidines, are much more resistant, being hardly attacked by nickel at 350°, but towards 500° there is elimination of ammonia with complete destruction of the molecule, according to a complicated reaction.[29]

[24] SABATIER and MAILHE, *Compt. rend.*, **150**, 1570 (1910).
[25] DEUSS, *Rec. Trav. Chim. Pays-Bas*, **27**, 145 (1908).
[26] HUGERSHOFF, *Berichte*, **32**, 2245 (1899).
[27] SABATIER and GAUDION, *Compt. rend.*, **165**, 309 (1917).
[28] SABATIER and GAUDION, *Compt. rend.*, **165**, 226 (1917).
[29] SABATIER and GAUDION, *Compt. rend.*, **165**, 309 (1917).

632. By heating α-*naphthylamine* for 8 hours with a molecule of *aniline* in presence of a small amount of iodine (less than 1 %), ammonia is eliminated and *phenyl-naphthylamine* is formed in 85 % yield.

The use of very small proportions of iodine enables us to prepare the secondary amines derived from α-naphthylamine and the three *toluidines, ortho* and *para anisidines,* and *meta* and *para chloranilines,* with yields superior to those obtained by the usual methods.

By heating β-*naphthylamine* on the steam bath for 4 hours with less than 1 % of iodine, it is almost quantitatively changed into ββ'-dinaphthyl-amine.

Likewise *p.aminophenol* heated below 200° for 5 hours with 0.0025 % iodine, loses ammonia and yields about 70 % *pp'.dihydroxy-diphenylamine.*[30]

633. **Cuprous chloride** and *bromide* and also *zinc chloride* catalyze the decomposition of the *phenylhydrazones* derived from the lower aliphatic aldehydes and ketones, giving ammonia and substituted *indols.*

Thus the phenylhydrazone of *methyl-ethyl-ketone* evolves ammonia at 180° when 0.2 % of cuprous chloride is added and yields *2, 3-dimethyl-indol* in 2 hours.

The phenylhydrazone of *propionic aldehyde* gives similarly *3-methyl-indol (skatol).* With copper chloride the yield is 60 % and reaches 73 % with zinc chloride.

With aldehydes there is some formation of nitriles resulting from splitting off aniline (635).

The formation of β-methyl-indol is thus represented:
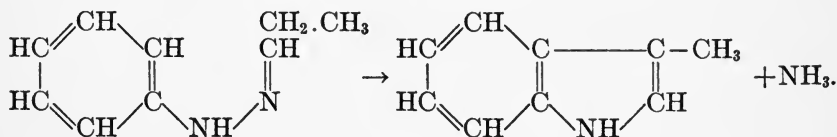
In the same way, the phenylhydrazone of *acetonyl-acetone* yields *dimethyl-amino-phenyl-pyrrol.*[31]

With the phenylhydrazones derived from higher aliphatic aldehydes, this reaction is of little importance as it is overshadowed by the formation of nitriles (635).

[30] KNOEVENAGEL, *J. prakt. Chem.* (2), **89**, 20 (1914).

[31] ARBUSOF and TIKHVINSKY, *J. Russian Phys. Chem. Soc.,* **45**, 73 (1913), *C. A.,* **7**, 2225. — ARBUSOF and FRIAUF, *Ibid.,* **45**, 694 (1913), *C. A.,* **7**, 3599. — ARBUSOF and KHRUTZKII, *Ibid.,* **45**, 699 (1913), *C. A.,* **7**, 3599.

§ 7. — ELIMINATION OF ANILINE

634. The stability of aniline in the presence of nickel, which has been mentioned above, enables us to predict that the action of nickel on alkyl anilines will tend to split off aniline, as ammonia is eliminated from the alkyl ammonias. This is what takes place with *methyl-aniline* at 250°. Aniline is regenerated with the separation of the group CH_2 which decomposes into methane and carbon, the reaction being nearly thus:

$$2C_6H_5.NH.CH_3 = 2C_6H_5.NH_2 + C + CH_4.$$

With *ethyl-aniline*, we have:

$$C_6H_5.NH.C_2H_5 = C_6H_5.NH_2 + C_2H_4,$$
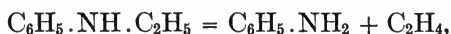
the ethylene being entirely decomposed by the nickel (912) into carbon, methane, ethane and hydrogen, the hydrogen acting on the aniline to give a little ammonia and benzene.

Dimethyl-aniline and *diethyl-aniline* behave in an entirely analogous manner.[32]

635. The phenylhydrazones of higher *aliphatic aldehydes* are decomposed by *copper, zinc,* and *platinum chlorides* into *nitriles* and *aniline*:

$$R.CH : N.NH.C_6H_5 = R.CN + C_6H_5.NH_2.$$
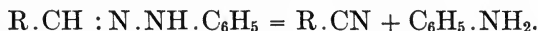
This is true for *isobutyric, isovaleric,* and *isoheptylic aldehydes*. The simultaneous production of *indols* (633) is of little importance.[33]

[32] SABATIER and GAUDION, *Compt. rend.,* **165,** 309 (1917).
[33] ARBUSOF, *J. Russian Phys. Chem. Soc.,* **45,** 74 (1913).

CHAPTER XIV

DEHYDROGENATION

636. We have explained direct hydrogenation by means of finely divided metals by the formation of an unstable hydride, produced rapidly by the metal and capable of readily giving up its hydrogen. If this explanation is correct, an important consequence can be readily foreseen. The catalytic metals, nickel, copper, and platinum, should be able to take up hydrogen not only from molecules of free hydrogen but also from other substances capable of furnishing hydrogen, and consequently to be *dehydrogenation catalysts*, a prediction which experiment has largely verified.

637. This capability has been long known in some cases. As early as 1823 it was known that *iron, copper, gold, silver,* and *platinum* had the power of greatly facilitating the decomposition of ammonia, without appreciable alteration of the metal. The decomposition of the ammonia can be thus effected at a much lower temperature than in the absence of these metals.[1]

In 1843, Reiset and Millon noticed that alcohol vapor passed through a tube filled with fragments of porcelain and heated to 300°, is not appreciably decomposed, but that decomposition manifests itself at 220° in presence of *platinum sponge.*[2]

In 1866, Berthelot noticed that the presence of iron favors the decomposition of *acetylene* at a red heat,[3] and later Schützenberger stated that *platinum sponge* warmed in a current of acetylene, decomposes it with incandescence, giving a voluminous mass of carbon in which the metal is diffused.[4]

This active decomposition of acetylene was rediscovered in 1896 by Moissan and Moureu, who observed it also with recently reduced iron, cobalt, and nickel.[5] A similar decomposition of *ethylene* in contact with the same metals at 300°, was obtained in 1897 by Sabatier and Senderens,[6] who interpreted it by assuming the temporary for-

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[1] Dulong and Thénard, *Ann. Chim. Phys.* (2), **23**, 440 (1823).

[2] Reiset and Millon, *Ann. Chim. Phys.* (3), **8**, 280 (1843).

[3] Berthelot, *Compt. rend.,* **62**, 906 (1866).

[4] Schützenberger, *Traité de Chemie,* I, 724.

[5] Moissan and Moureu, *Compt. rend.,* **122**, 1241 (1896).

[6] Sabatier and Senderens, *Compt. rend.,* **124**, 616 (1897).

mation of a metal hydride and were thus led to apply these metals to dehydrogenation reactions as well as to those of hydrogenation.

638. The dehydrogenation catalysts are primarily the *metals*, and to a less degree, certain *anhydrous metal oxides* and some salts derived from these oxides, *carbon* and, in exceptional cases, *anhydrous aluminum chloride*.

The effects produced by these catalysts can be divided into several groups:

1. Dehydrogenation of hydrocarbons.
2. Return of *hydroaromatic* compounds to aromatic with double bonds.
3. Conversion of primary alcohols to aldehydes and of secondary to ketones.
4. Dehydrogenation of poly-alcohols.
5. Dehydrogenation of amines to nitriles.
6. Direct synthesis of amines from hydrocarbons.
7. Formation of rings by loss of hydrogen.

§ 1. — DEHYDROGENATION OF HYDROCARBONS

639. Finely divided metals exercise an important dehydrogenating effect on hydrocarbons, the effect being greater the higher the temperature. The separation of hydrogen is always accompanied by molecular changes, which are frequently followed by condensation into more complex hydrocarbons. We will return to the breaking down and building up of hydrocarbons by catalysts in Chapter XXI, which is devoted to that subject, and will content ourselves in the following paragraph to the regular passage of hydroaromatic hydrocarbons to the aromatic with double bonds.

§ 2. — DEHYDROGENATION OF HYDROAROMATIC COMPOUNDS

640. The various compounds formed by the hydrogenation of *stable* cyclic compounds tend to revert to the latter by loss of hydrogen when submitted to the action of finely divided metals at temperatures higher than those at which they are formed directly. Among the metals, reduced *nickel* shows itself as particularly active.[7]

The dehydrogenation can take place in the presence of excess of hydrogen, and in some cases the excess of hydrogen, *far from hinder-*

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[7] This is probably a reversible reaction reaching a definite equilibrium for each temperature and pressure of hydrogen. Quantitative studies are most desirable. — E. E. R.

ing the reaction, regulates it by favoring the maintenance of the cyclic structure and diminishing the tendency to the breaking up of the molecule into many fragments (644).

641. **Cyclohexane,** which can not be formed by the direct hydrogenation of benzene by the aid of nickel above 300° (446), suffers a partial dehydrogenation to benzene above 300°, but a part of the benzene is transformed to *methane* by the liberated hydrogen: [8]

$$3C_6H_{12} = 2C_6H_6 + 6CH_4.$$

The presence of a current of hydrogen stabilizes the molecule to a certain extent so that it is only slightly broken up at 350°. At 400° about 30 % of the cyclohexane passing over the nickel with the hydrogen is decomposed into benzene. [9]

With *methyl-cyclohexane* alone, decomposition begins at 240° and is rapid at 275°, the gas evolved then containing:

$$\text{Methane} \dots \dots \dots \quad 78\,\% \text{ by volume}$$
$$\text{Hydrogen} \dots \dots \dots \quad 22\,\% \text{ by volume}$$

The condensed liquid contains a large proportion of toluene.

Ethyl-cyclohexane is attacked slowly at 280 to 300° and gives a gas containing 83 % methane and 17 % hydrogen, a mixture of *ethyl-benzene* and *toluene* being condensed.

The *1, 3-dimethyl-cyclohexane* acts like cyclohexane and is stabilized by an excess of hydrogen. At 400°, the dehydrogenation to *m.xylene* does not exceed 25 %. [10]

Reduced copper exercises a similar but less intense action which does not begin till above 300°.

642. Hydroxy and amino substitution products of cyclohexane hydrocarbons undergo dehydrogenation still more readily and above 350° the reaction is not hindered by an excess of hydrogen.

In the presence of nickel above 350°, *cyclohexanol* and its homologs come back to the *phenol* condition. This effect commences at even much lower temperatures: when *cyclohexanone* is hydrogenated over nickel at 230°, 25 % of *phenol* is collected along with the cyclohexanol. [11] In a current of hydrogen at 360° the transformation into phenol is practically complete. [12]

The same effect is even more important for the cyclic *poly-alcohols* and also for the amines such as *cyclohexyl-amine* which tends to regen-

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[8] Sabatier and Mailhe, *Compt. rend.,* **137,** 240 (1903).

[9] Sabatier and Daudier, *Compt. rend.,* **168,** 670 (1919).

[10] Sabatier and Gaudion, *Unpublished results.*

[11] Skita and Ritter, *Berichte,* **44,** 668 (1911).

[12] Padoa and Fabris, *Lincei,* **17** (1), 111 and 125 (1908), *C.,* **1908** (1), 1395 and **1908** (2), 1103.

erate aniline and *dicyclohexyl-amine* which yields *diphenylamine* and *cyclohexylaniline.*

The *hydrides* of *naphthalene* act in the same way: the higher hydrides under the influence of nickel at 200° come back to the *tetrahydride,* and this regenerates naphthalene at 300°.

Frequently, as in the case of cyclohexane, the liberated hydrogen can break down a portion of the hydrocarbon into larger or smaller aliphatic fragments. This takes place with *dodecahydrophenanthrene,* which breaks down at 200° into lower hydrides and various aliphatic hydrocarbons, while the *hexahydride* is regularly dehydrogenated to the *tetrahydride* at 220°, which in turn passes to phenanthrene at 280°.

With nickel at 300–330°, the perhydrides of anthracene give the tetrahydride and decomposition products

At 250°, *decahydrofluorene* returns to fluorene.

643. Unsaturated cyclic hydrocarbons, *cyclohexenes, cyclohexadienes,* as well as the *terpenes* and various of their substitution products, are still more readily dehydrogenated by nickel even in a current of hydrogen.

Cyclohexene gives *benzene* almost quantitatively when passed over nickel at 250°.[12] The same is true at 300° in a current of hydrogen.[13]

Cyclohexadiene, C_6H_8, passed over finely divided platinum at 180°, yields benzene, but this is mixed with *cyclohexane,* which is stable at this temperature and which results from the utilization of the liberated hydrogen.[14]

644. **Limonene,** in a current of hydrogen over nickel at 280–300°, is changed almost entirely into *cymene* accompanied by a certain amount of *cumene* and simpler aromatic hydrocarbons.

Menthene, in hydrogen over nickel at 360°, yield 80 % of cymene.

Under the same conditions, *pinene* and *camphene* are dehydrogenated to aromatic hydrocarbons, $C_{10}H_{14}$ and lower.[15]

645. **Eucalyptol,** or cineol, $CH_3 . C \underset{\displaystyle \overset{|}{\underset{}{\rule{0pt}{0pt}}}}{\overset{\displaystyle /CH_2.CH_2\backslash}{\backslash CH_2.CH_2/}} CH . C \overset{/CH_3}{\underset{\overset{|}{O}\backslash CH_3}{}}$, carried
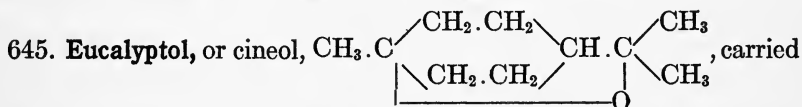
along by a current of hydrogen over nickel at 360° is simultaneously reduced and dehydrogenated to form *cymene.*

Terpineol undergoes a similar reaction.

Pulegone, $CH_3 . CH \overset{\displaystyle /CH_2.CO\backslash}{\underset{\displaystyle \backslash CH_2.CH_2/}{}} C : C \overset{/CH_3}{\backslash CH_3}$, submitted to the action
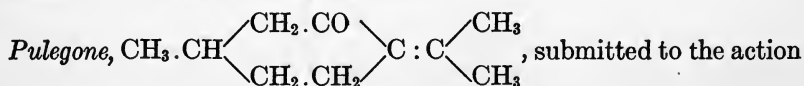
[13] SABATIER and GAUDION, *Compt. rend.,* **168,** 670 (1919).
[14] BÖESEKEN, *Rec. Trav. Chim. Pays-Bas,* **37,** 255 (1918).
[15] SABATIER and GAUDION, *Compt. rend.,* **168,** 670 (1919).

of nickel in a current of hydrogen at 360°, is changed into a mixture of *thymol* and *cresol*, formed by the elimination of the carbon chain in the form of methane.[15]

646. **Dodecahydrotriphenylene** is completely changed to *triphenylene*, melting at 198°, by passing over copper at 450–500°.[16]

647. **Piperidine,** under the action of nickel at 180 to 250°, even in the presence of hydrogen, is totally changed to pyridine:[17]

$$CH_2 \begin{array}{c} /CH_2.CH_2 \backslash \\ \backslash CH_2.CH_2 / \end{array} NH \rightarrow CH \begin{array}{c} /CH:CH \backslash \\ \backslash CH:CH / \end{array} N.$$
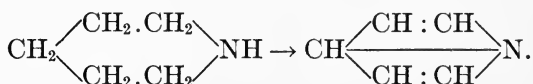
Tetrahydroquinoline, passed over nickel at 180°, gives a certain proportion of quinoline, but the chief product is skatol:[18]
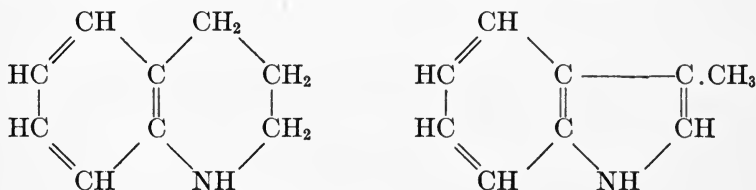
648. If dehydrogenation is carried out with a partially hydrogenated product, the hydrogen set free by the action of the metal on one portion may hydrogenate the other. This is what takes place when *palladium* sponge acts on *methyl tetrahydroterephthalate* which gives 1 part *methyl terephthalate* and 2 parts *methyl hexahydroterephthalate*.[19]

649. **Palladium black** is an active dehydrogenation catalyst for the *hexamethylene hydrocarbons*. The action begins at 170°, is vigorous at 200°, at a maximum at 300°, and yields only hydrogen and *benzene* or its homologs. At 100–110°, the inverse action takes place, *i.e.* there is hydrogenation of the benzene, but this does not take place at 200° even in excess of hydrogen. Likewise *hexahydrobenzoic* acid passes to *benzoic*.[20] The esters of *hexahydrobenzoic* acid are also dehydrogenated, but *methyl cyclopentane-carbonate* is not affected.[21]

[16] MANNICH, *Berichte,* **40,** 159 (1906).
[17] CIAMICIAN, *Lincei,* **16,** 808 (1907).
[18] PADOA and SCAGLIARINI, *Lincei,* **17** (1), 728 (1908), *C.,* **1908** (2), 614.
[19] ZELINSKY and GLINKA, *Berichte,* **44,** 2305 (1911).
[20] ZELINSKY and MISS UKLONSKAJA, *Berichte,* **45,** 2677 (1912).
[21] ZELINSKY and MISS UKLONSKAJA, *J. Russian Phys. Chem. Soc.* **46,** 56 (1913), *C. A.,* **7,** 2224.

Below 300°, *cyclopentane* and *methyl-cyclopentane* [22] and *cycloheptane* [23] are not dehydrogenated.

Platinum black acts similarly but less energetically.[23]

§ 3. — DEHYDROGENATION OF ALCOHOLS

650. A long time ago Berthelot noticed that the vapors of ethyl alcohol passed through a progressively heated glass tube, begin to decompose at around 500°, that is at nearly a dull red heat, giving rise to two simultaneous reactions, namely: *dehydration* with separation of ethylene and *dehydrogenation* with the production of aldehyde, the reactions being further complicated by the decomposition of the ethylene and the aldehyde by the heat, the aldehyde being partially decomposed into carbon monoxide and methane.[24]

Various *primary* alcohols undergo analogous decompositions at a dull red heat, being simultaneously dehydrated and dehydrogenated. We have:

$$C_nH_{2n+1}.CH_2.CH_2OH \begin{cases} \nearrow H_2O + \underbrace{C_nH_{2n+1}.CH:CH_2}_{\text{ethylene hydrocarbon}} \\ \searrow H_2 + \underbrace{C_nH_{2n+1}.CH_2.CO.H}_{\text{aldehyde}} \end{cases}$$

and likewise:

$$\underbrace{C_6H_5.CH_2OH}_{\text{benzyl alcohol}} \begin{cases} \nearrow H_2O + (C_6H_5.CH)_x \\ \searrow H_2 + \underbrace{C_6H_5.CO.H}_{\text{benzaldehyde}} \end{cases}$$
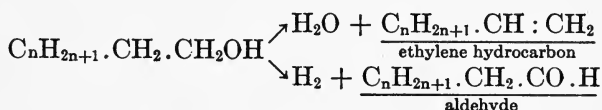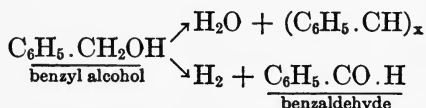
Up to 400°, neither of these reactions takes place to any appreciable extent.

Secondary alcohols react more readily in this manner, giving *hydrocarbons* by dehydration and *ketones* by dehydrogenation, the one or the other reaction predominating as the case may be. Thus, for secondary aliphatic alcohols, ethylene hydrocarbons are formed rather than ketones, while *benzhydrol* yields benzophenone at as low as 290°.[25]

651. In the presence of *catalysts*, that is to say of substances capable of forming temporary chemical combinations with one of the products of the above reactions, the corresponding reaction will be realized at a lower temperature and rendered more or less rapid.

[22] ZELINSKY, *J. Russian Phys. Chem. Soc.*, **43**, 1220 (1911). — *Berichte*, **45**, 3678 (1912).

[23] ZELINSKY and HERZENSTEIN, *J. Russian Phys. Chem. Soc.*, **44**, 275 (1912).

[24] BERTHELOT and JUNGFLEISCH, *Traité élém. de Chimie Org.*, 2nd. Ed. Paris, 1886, I, 256.

[25] KNOEVENAGEL and HECKEL, *Berichte*, **36**, 2816 (1903).

Dehydrogenation catalysts should specially promote the decomposition of alcohols into aldehydes or ketones, while *dehydration catalysts* should facilitate the formation of water and hydrocarbons.

The metals, *copper, cobalt, nickel, iron, platinum,* and *palladium,* particularly in the finely divided form, are *dehydrogenation* catalysts, and so are a small number of anhydrous oxides, *e.g. manganous,* though to a less extent.

On the contrary, certain metal oxides are exclusively *dehydration* catalysts for alcohols: such are *thoria, alumina* and the *blue oxide* of *tungsten.*

Finally a large number of substances, oxides and salts, have both functions and can to very variable extents cause the dehydration and the dehydrogenation of alcohols at the same time. *Beryllia* and *zirconia* play the two rôles almost equally well; all the intermediates are found between the two extremes of exclusive catalysts.[26]

652. Of all the dehydrogenation catalysts, the one that serves best for the regular decomposition of primary or secondary alcohols into aldehydes or ketones, is *reduced copper,* which in practice can be replaced by the very finely divided copper which is manufactured fo imitation gilding.

Cobalt, iron, and *platinum* can be used, but with poorer results, while *nickel* is the least suitable.[27]

Use of Copper

653. **Primary Alcohols.** Primary aliphatic alcohols, when passed in the vapor form over reduced copper kept between 200 and 300°, are regularly decomposed into aldehydes and hydrogen, the condensate containing, along with the aldehyde, some of the unchanged alcohol and a little of the corresponding acetal. The practical yield is usually above 50 % with less than 5 % of higher products and 45 % of the alcohol which can be fractioned out and put through again. This is a very advantageous method for the preparation of *aliphatic aldehydes,* particularly for those which, on account of low volatility, are difficult to prepare by oxidation of the alcohols.

The transformation can never be complete, even when a long train of copper is used, since the hydrogen which is formed can be added to the aldehyde by copper above 200°. Hence the reaction is limited but the conditions are favorable to the decomposition because the operation is carried on in the presence of a small concentration of hydrogen.

By operating under reduced pressure, there is the double advantage of a more ready volatilization of the alcohols and a diminution

[26] SABATIER and MAILHE. *Ann. Chim. Phys.* (8), **20**, 289 and 341 (1310).
[27] SABATIER and SENDERENS, *Compt. rend.,* **136**, 738, 921 and 983 (1903).

of the reverse action of hydrogen, and consequently increasing the practical yield.

654. The apparatus used by Sabatier and Senderens is the same as that employed for hydrogenations (347) except that the tube for introducing the hydrogen is omitted.[28]

Bouveault has used a vertical tube for the catalyst, 25–30 mm. in diameter and of varying length, up to 1 m. The lower extremity which is drawn down to 10 mm. passes through the stopper of a flask in which the alcohol is vaporized. The tube is filled with rolls of copper gauze containing copper hydroxide, resembling cigarettes; it is heated by a coil of resistance wire through which passes a current that can be suitably regulated. The reduction of the copper hydroxide is effected by hydrogen at 300° and should be carried on slowly so as to leave an adherent mass of copper.

The current is regulated so as to obtain the desired temperature and the alcohol vapors pass through the vertical catalyst tube and from it into a fractionating column which separates the more volatile aldehyde and returns the less volatile alcohol to the flask to be revaporized. A catalyst tube 1 m. long is sufficient for the preparation of 500 g. aldehyde in a day.[29] [30]

It is evident that the apparatus may be connected with a pump controlled by a regulator so as to operate in a partial vacuum, if this is desired.

655. If the temperature is above a certain point, the aldehydes formed are partially destroyed by contact with the metal with elimination of carbon monoxide:

$$R.CO.H = CO + RH.$$

But except in the case of formaldehyde and the aromatic aldehydes, this decomposition is not yet rapid at 300°.

This decomposition is more rapid with a more active catalyst. With methyl alcohol, using a light violet copper prepared by the slow reduction of the precipitated oxide, there is a rapid evolution of gas which contains about 1 volume of carbon monoxide to 2 of hydrogen: the formaldehyde produced has been completely destroyed, only traces of it being found in the condensate. We have:

$$H.CH_2.OH = CO + 2H_2.$$
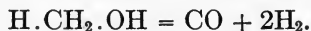
On the contrary with compact reddish orange copper, prepared by reducing a dense oxide at a dull red, the evolution of gas is only about

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[28] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 332 (1905).

[29] BOUVEAULT, *Bull. Soc. Chim.* (4), **3**, 50 and 119 (1908).

[30] This apparatus and its operation are more fully described by WEISMANN and GARRAND, *J. Chem. Soc.*, **117**, 328 (1920). — E. E. R.

one twelfth as rapid, but it is practically pure hydrogen and almost all of the formaldehyde survives.[31]

656. Methyl alcohol is decomposed even at 200° and very rapidly at 280–300°.

By catalytic decomposition over copper, methyl alcohol can be detected in ethyl alcohol, since the formaldehyde produced can be characterized by the violet coloration which it gives with morphine and concentrated sulphuric acid.[32]

The destruction of the formaldehyde is already apparent at 240–260°, hydrogen and carbon monoxide being produced along with a little methyl formate (225),[33] this destruction increasing rapidly with rise of temperature, till at 400° at least 75 % is decomposed.

Ethyl alcohol is decomposed above 200°, the aldehyde being formed rapidly at 250 to 350°, without complications. At 420°, 16 % of the acetaldehyde is destroyed and the gas collected contains 3 volumes of methane and 1 of carbon monoxide to 6 of hydrogen.[34]

Propyl alcohol is transformed regularly at 230 to 300° and at 420° one fourth of the aldehyde is destroyed.

Butyl alcohol yields the aldehyde well at 220 to 280°, and at 370° only one sixth is destroyed.

At 240 to 300°, *isobutyl alcohol* is easily transformed into the aldehyde: at 400°, one half of this is decomposed.

Isoamyl alcohol yields the aldehyde at 240 to 300° without complications. At 370° only 6 % of the product is decomposed and at 430°, about 25 %.[35]

An aliphatic C_{10} alcohol is regularly changed into the aldehyde by heating in Bouveault's apparatus under reduced pressure.[36]

The copper is never fouled by carbonaceous deposits and remains able to continue the reaction indefinitely.

657. Benzyl alcohol is transformed less readily than the aliphatic: the decomposition does not begin below 300° but is satisfactory there. At 380° the reaction is complex and some *toluene* and *benzene* are formed along with the *benzaldehyde*, while the gases evolved contain carbon monoxide and dioxide along with the hydrogen. From 18 parts of alcohol, only 13 go to the aldehyde, the other 5 forming benzene and toluene.

Under reduced pressure, *phenylethyl alcohol*, $C_6H_5.CH_2.CH_2OH$,

[31] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 344 (1910).

[32] MANNICH and GEILMANN, *Arch. Pharm.*, **254**, 50 (1916), *C. A.*, **11**, 1114.

[33] MANNICH and GEILMANN, *Berichte*, **49**, 585 (1916).

[34] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 463 (1905).

[35] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 463 (1905).

[36] BOUVEAULT, *Bull. Soc. Chim.* (4), **3**, 50 and 119 (1908).

yields *phenyl-acetaldehyde* readily, but there is a little decomposition of the aldehyde into *toluene* and carbon monoxide and there is also some dehydration of the alcohol to *styrene*, $C_6H_5 . CH : CH_2$, the major part of which is hydrogenated to *ethyl-benzene* or condensed to the slightly volatile *meta-styrene* which remains on the metal and weakens its catalytic activity.

658. The unsaturated *allyl alcohol*, $CH_2 : CH . CH_2OH$, is transformed over copper at 180 to 300°, with the evolution of very little hydrogen, into *propionic aldehyde*, with a slight amount of acroleïne. The hydrogen derived from the decomposition of the alcohol serves to hydrogenate the double bond of the aldehyde formed (432).[35]

It is the same way with *undecenyl alcohol*, $CH_2 : CH . (CH_2)_8 .- CH_2OH$, which yields only the saturated aldehyde, *undecenal*. On the contrary, under reduced pressure, *geraniol* (416) gives *citral* almost entirely.[36]

659. **Secondary Alcohols.** The transformation of secondary alcohols into ketones with the separation of a molecule of hydrogen is even more readily accomplished by finely divided *copper* since, the ketones being more stable than the aldehydes, a larger temperature interval is available in which to effect the transformation. Usually even at 400° there is no appreciable complication, the gas evolved is pure hydrogen. The immediate yield of ketone may exceed 75%.

As in the case of the aldehydes, the reaction is never entirely complete, since, in contact with copper above 200°, the disengaged hydrogen is capable of hydrogenating the ketone to regenerate the alcohol. But the hydrogenating power of the copper is much less than its aptitude to decompose the alcohol and the production of ketone predominates greatly.[37]

Isopropyl alcohol is decomposed slowly from 150°, the production of *acetone* being rapid at 250 to 430°, without separation of propylene.

Secondary *butyl alcohol* is attacked at 160°, and furnishes *butanone* readily at 300° without production of *butylene*.

Secondary *octyl alcohol* produces only the *octanone* (*2*) at 250 to 300°. It is only above 400° that there is decomposition into carbon monoxide and hydrocarbons.

660. Over copper at around 300°, *cyclohexanol* is split cleanly into hydrogen and cyclohexanone.[37]

At 300°, *o.methyl-cyclohexanol* is transformed into *o.methyl-cyclohexanone*, with a little water and *o.methyl-cyclohexene* and some *o.cresol* which are readily eliminated. Results almost as good are obtained with the *meta* but less satisfactory with *p.methyl-cyclohexanol*.

[37] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 467 (1905).

The method may be used with the same facility with the various *dimethyl-cyclohexanols*.[38]

661. By contact with copper at 300°, *borneol* is changed very readily and almost totally into *camphor*.[39]

662. **Benzhydrol.** $C_6H_5.CH(OH).C_6H_5$, when its vapors are passed over copper at 350°, yields *benzophenone*, which is largely changed by the liberated hydrogen into *diphenyl-methane* and particularly into symmetrical *tetraphenyl-ethane* (720).

663. The method is suitable for transforming a secondary alcohol group into a ketone group even in mixed compounds. The secondary alcohol-ketones of the form $R.CH(OH).CO.R'$ readily furnish the corresponding α-diketones.[40]

Under the same conditions, *β-hydroxy-esters* can be transformed into *ketone-esters*. Thus *ethyl β-hydroxy-isoheptoate*, $(CH_3)_2CH.CH_2.-CH(OH).CH_2CO_2C_2H_5$, is changed to *ethyl β-keto-isoheptoate*.[41]

Use of Other Metals

664. **Nickel.** Reduced nickel acts more violently on the alcohols than does copper and the dehydrogenation of primary or secondary alcohols is always accompanied by a more or less considerable splitting up of the aldehyde or ketone, with the formation of carbon monoxide which may be more or less profoundly altered by the nickel; a part being hydrogenated by the hydrogen formed from the alcohol and a part being changed to carbon and carbon dioxide (614). The separation of the carbon monoxide usually begins at the same time as the decomposition of the alcohol.[42]

Methyl alcohol is attacked as low as 180°, but two thirds of the liberated formaldehyde is destroyed. The reaction is rapid at 250° but eight ninths of the aldehyde is destroyed and the gas evolved contains only 45 % of hydrogen along with methane and carbon monoxide. At 350° there is no longer any aldehyde and no carbon monoxide : the gas is a mixture of methane and carbon dioxide.

Ethyl alcohol is decomposed from 150° up, rapidly above 230°. As low as 180°, almost a third of the aldehyde formed is decomposed, and at 330° its destruction is complete.

[38] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **10**, 550, 554, 557 and 568 (1907).

[39] GOLDSMITH, *English patent*, 17,573 of 1906; *J. S. C. I.*, **26**, 777 (1907). — ALOY and BRUSTIER, *Bull. Soc. Chim.* (4), **9**, 733 (1911).

[40] BOUVEAULT and LOCQUIN, *Bull. Soc. Chim.* (3), **35**, 650 (1906).

[41] BOUVEAULT, *Loc. cit.*

[42] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 469 (1905).

The results are similar with *propyl alcohol*, with which 75 % of the aldehyde is decomposed at 260°; and with *n.butyl alcohol* with which 92 % of the aldehyde is decomposed; and for *isobutyl alcohol*. With ordinary *isoamyl alcohol*, the destruction of the aldehyde already reaches one half at 210°.

Heptyl alcohol, submitted to the action of nickel at 220°, gives only a small amount of the aldehyde, the chief product being hexane resulting from its decomposition with separation of carbon monoxide.[43]

665. In contact with nickel, *isopropyl alcohol* is slowly decomposed into acetone and hydrogen from 150° up. The reaction is rapid at 210° but about 12 % of the alcohol that is transformed is split into water, ethane and methane.

Secondary *butyl alcohol* is transformed quite regularly above 200° but 20 % of the product is already decomposed, while at 310°, 80 % is destroyed.

For *methyl-hexyl-carbinol* the decomposition is clean at 250° but at that temperature already the methyl-hexyl-ketone formed is mostly broken down into carbon monoxide, methane and hexane, only a third surviving.

666. **Cobalt.** The action of reduced cobalt on primary and secondary alcohols is between that of nickel and that of copper.[44]

667. **Iron.** The action of iron is analogous to that of cobalt. At high temperatures, 600 to 700°, it causes a rapid destruction. An iron tube either empty or filled with iron turnings decomposes ethyl alcohol strongly at 700° giving 30 % aldehyde and depositing about 7 % of carbon.[45]

668. **Platinum.** Platinum sponge acts on alcohols as does nickel but its action does not begin till above 250°. Besides the destruction of the *aldehydes* is inseparable from their formation and always predominates.

Around 250° *methyl alcohol* is split cleanly into hydrogen and carbon monoxide with no methane and only traces of formaldehyde.

Ethyl alcohol is attacked at 270°, and at 370° the reaction is rapid, but 75 % of the aldehyde is decomposed into carbon monoxide and methane.

Propyl alcohol is split above 280°, but at 310° the aldehyde is almost completely decomposed into ethane and carbon monoxide.

The results are better with secondary alcohols since the ketones are more stable than the aldehydes.

[43] BOESEKEN and VAN SENDEN, *Rec. Trav. Chim. Pays-Bas*, **32**, 23 (1913).
[44] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 473 (1905).
[45] IPATIEF, *Berichte*, **35**, 1047 (1902).

Isopropyl alcohol is transformed into *acetone* at 320° without notable complications and at 400° the destruction of the acetone reaches barely 3 % of the product.[46]

669. **Palladium.** The considerable affinity that this metal has for hydrogen seems to fit it for the dehydrogenation of alcohols. *Benzhydrol* is rapidly decomposed into benzophenone by contact with *palladium sponge*.[47]

670. **Zinc.** Around 650° this metal decomposes alcohols strongly : *ethyl alcohol* yields 60 % aldehyde and the gases, ethylene, carbon monoxide and methane. *Isobutyl alcohol* gives 75 % of aldehyde and gas which is largely butylene.

Brass, an alloy of copper and zinc, acts at 600° like zinc.[48]

Use of Other Materials

671. The use of other substances to dehydrogenate alcohols is not advantageous since they act much less energetically than the metals and because they require the use of higher temperatures at which the aldehydes are decomposed into carbon monoxide and saturated hydrocarbons.

672. **Manganous Oxide.** Its action hardly begins below 320°. At 360° it decomposes *methyl alcohol* only one sixth as rapidly as compact red-orange copper; the greater part of the formaldehyde survives and the hydrogen is nearly pure.

At 360° the decomposition of *ethyl alcohol* is only one fortieth as rapid as with light copper and a part of the aldehyde is already decomposed into ethane, carbon monoxide and even carbon dioxide, the latter being formed from the carbon monoxide with a corresponding deposit of carbon, the reaction being similar to that produced by metals (614).

Propyl, isoamyl and *benzyl alcohols* give analogous results.[49]

673. **Stannous Oxide.** This acts above 300° as a dehydrogenation catalyst after the manner of the metals, but is *slowly* reduced meanwhile into metallic tin, which is easy to see in the oxide. This finely divided tin seems to possess a catalytic power similar to that of the oxide so that the mixture of metal and oxide continues to split alcohols into aldehydes and hydrogen for a long time, but as the reaction temperature is above 220°, the melting point of tin, the tiny globules

[46] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 473 (1905).

[47] KNOEVENAGEL and HECKEL, *Berichte,* **36,** 2816 (1903).

[48] IPATIEF, *Berichte,* **34,** 3579 (1901) and **37,** 2961 and 2986 (1904).

[49] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20,** 313 (1910).

of metal resulting from the reduction of the oxide gradually coalesce into larger, and consequently the activity diminishes.

Thus with *ethyl alcohol*, the brownish orange stannous oxide (resulting from the reduction of stannic oxide by the alcohol vapors) commences to act at 260°. At 350° the velocity of the reaction is almost half as great as with the same volume of very light *reduced copper*. The disengaged hydrogen is almost pure, the acetaldehyde being only slightly decomposed. At the end of four hours the velocity of the reaction is reduced by half.

Amyl alcohol yields the aldehyde regularly at 340°.

Methyl alcohol is attacked above 260° with the production of formaldehyde. At 350° the most of this is decomposed into carbon monoxide and hydrogen.[50]

674. Cadmium Oxide. This behaves like stannous oxide and dehydrogenates while it is reduced at the same time to the metal which possesses a catalytic activity differing little from that of the oxide. Thus with *ethyl alcohol* at 300° the reaction is about one tenth as rapid as with the same volume of very active copper and maintains itself for a long time in spite of the progressive reduction of the oxide.

Benzyl alcohol acts in exactly the same way : at 350° there is a slow reduction of the oxide and at the same time a splitting of the alcohol into benzaldehyde and hydrogen. At 380° the *benzaldehyde* is partially decomposed into benzene and carbon monoxide. The entire absence of the resinous hydrocarbon (714) indicates that there is no dehydration.

With *methyl alcohol*, the splitting which begins at 250° is quite rapid above 300° and produces formaldehyde which is partially decomposed into carbon monoxide and hydrogen.[51]

675. Other Oxides. Most *non-reducible* metallic oxides are *mixed catalysts* for alcohol, causing dehydration and dehydrogenation at the same time. For some : uranous oxide, blue oxide of molybdenum, vanadous oxide, V_2O_3, zinc oxide, dehydrogenation predominates.

In another group : beryllium oxide, zirconium oxide, chromic oxide, Cr_2O_3 (calcined above 500°), the dehydrogenating and dehydrating powers are about equal.

For a third group : chromic oxide, Cr_2O_3 (not calcined), titanium oxide, silicon dioxide, dehydration predominates.

676. With reference to *methyl alcohol* the classification of the oxides is quite different since in this case dehydration can not take place except by the formation of methyl ether and the conditions are

[50] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20,** 309 (1910).
[51] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20,** 302 (1910).

not comparable. Except *alumina*, which at 390° only dehydrates, and several oxides (*thoria, blue oxide of tungsten, chromic oxide* and *alumina* above 350°) which are mixed catalysts, all metallic oxides dehydrogenate methyl alcohol with the production of *formaldehyde* which is more or less decomposed into carbon monoxide and methane.

The following table indicates the volume of gas obtained per minute with the same volume of various catalysts employed under the same conditions.

Oxides	Volume of gas in cc. per minute.

Formaldehyde remaining almost entirely; the gas is nearly pure hydrogen.

BeO	very small
SiO$_2$	0.3
TiO$_2$	1.2
ZnO	1.5
ZrO$_2$	1.8
MnO	2.0
Al$_2$O$_3$	6.0

Formaldehyde partially decomposed, the hydrogen contains carbon monoxide.

PbO [52]	45 (beginning)
Mo$_2$O$_3$	54
CdO	57 (beginning)

Formaldehyde almost completely destroyed, the gas is nearly $CO + 2H_2$.

Fe$_2$O$_3$ [52]	106 (beginning)
V$_2$O$_5$	140
SnO [52]	160 (beginning)
Light copper	152

677. The dehydrogenating power of oxides can hardly be explained except by assuming an unstable combination of the oxide and the aldehyde.[53]

678. **Zinc powder,** which is an intimate finely divided mixture of metallic zinc and zinc oxide, usually containing a certain proportion of cadmium and cadmium oxide, acts by virtue of these various substances as a quite active dehydrogenation catalyst, particularly toward *methyl alcohol,* the formaldehyde being mostly decomposed into carbon monoxide and hydrogen. Long ago Jahn noted that zinc powder splits methyl alcohol into a gas containing 30 % carbon monoxide and 70 % hydrogen.[54]

[52] The gas volumes given are taken after the absorption of the carbon dioxide resulting from the slow reduction of the oxide.

[53] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20,** 340 to 346 (1910).

[54] JAHN, *Berichte,* **13,** 983 (1880).

679. Carbon. Baker's coals act towards alcohols as a mixed catalyst causing dehydrogenation and dehydration simultaneously.

Ethyl alcohol undergoes a complex reaction at 375–385°, being almost completely destroyed yielding methane and carbon monoxide.

With *isopropyl alcohol* dehydration predominates.[55]

§ 4. — DEHYDROGENATION OF POLY-ALCOHOLS

680. Glycerine is the only poly-alcohol of which the dehydrogenation has been studied. When its vapors are passed at 330° over very light reduced *copper*, prepared by the reduction of cupric carbonate at a low temperature, there is a rapid evolution of gas consisting of hydrogen mixed with methane, carbon monoxide and dioxide, the proportion of the latter rising to one third of the whole.

The initial effect of the copper is dehydrogenation to *glyceric aldehyde:*

$$CH_2OH . CHOH . CH_2OH = H_2 + CH_2OH . CHOH . CHO.$$

As soon as this is formed it is decomposed in the same way as it is by beer yeast into *ethyl alcohol* and *carbon dioxide:* [56]

$$CH_2OH . CHOH . CHO = CO_2 + CH_3 . CH_2OH.$$
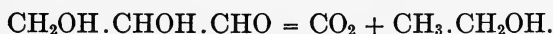
A part of this alcohol is found in the distillate and a part suffers dehydrogenation by the copper to *acetaldehyde*, $CH_3 . CHO$, which itself splits up, more completely when the temperature is high, into methane and carbon monoxide.

Furthermore, at the temperature of the reaction a portion of the glycerine is dehydrated to *acroleïne*, which is mostly found in the distillate with the alcohol and water but a part of which is hydrogenated by the copper to *propionic aldehyde, allyl alcohol* and *propyl alcohol* accompanied by condensation products due to the crotonization of the aldehydes. Ethyl alcohol is the chief constituent of the liquid.[57]

§ 5. — DEHYDROGENATION OF AMINES

681. Primary Amines. We have seen that *nickel* permits us to add hydrogen to nitriles at 200° to form *primary amines* (426). We may expect that it will reverse this reaction at higher temperatures and take hydrogen away from a primary amine derived from a *primary alcohol*, to reform the *nitrile:*

$$R . CH_2 . NH_2 = 2H_2 + R . CN.$$
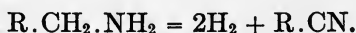
[55] Lemoine, *Bull. Soc. Chim.* (4), **3**, 851 and 935 (1908).
[56] Grimaux, *Bull. Soc. Chim.* (2), **49**, 251 (1888).
[57] Sabatier and Gaudion, *Compt. rend.*, **166**, 1037 (1918).

This is what takes place with *benzyl-amine*, with *amyl-amine* as well as with other primary aliphatic amines derived from primary alcohols having at least five carbon atoms.[58]

When the vapors of *benzyl-amine* alone are passed over a layer of reduced nickel maintained at 300–50°, *benzonitrile*, $C_6H_5.CN$, is formed. But at this temperature the liberated hydrogen reacts with the amine to give *toluene* and *ammonia* (496), so that the evolution of gas is a minimum. We may write the reaction:

$$3C_6H_5.CH_2.NH_2 = C_6H_5.CN + 2C_6H_5.CH_3 + 2NH_3.$$

The yield of benzonitrile is about one third.

Likewise at 300° *isoamyl-amine* yields *isobutyl cyanide* according to the reaction:

$$3(CH_3)_2CH.CH_2.CH_2.NH_2 = (CH_3)_2CH.CH_2.CN + 2C_5H_{12} + 2NH_3.$$

The *isopentane* produced is partially destroyed by the nickel, depositing carbon and liberating hydrogen and lower hydrocarbons.

The reaction goes poorly with amines derived from primary alcohols having less than five carbon atoms, since with these amines nickel has a strong tendency to eliminate ammonia with the formation of *ethylenic hydrocarbons* (631).[59]

When copper is used in place of nickel between 390 and 400°, much more complex products are obtained somewhat similar to those obtained by the hydrogenation of aliphatic nitro compounds (510).

682. Secondary and Tertiary Amines. Secondary and tertiary amines derived from primary alcohols also furnish *nitriles* when passed over nickel at 320–50°, by the simultaneous elimination of hydrogen and *ethylenic hydrocarbons*. Thus from *di-isoamyl-amine* and *tri-isoamyl-amine*, *isobutyl cyanide* is obtained.[60]

§ 6. — SYNTHESIS OF AMINES

683. When a mixture of *ammonia* and *benzene* vapor is heated to 550° without catalyst, a slight formation of *aniline* is observed according to the reaction:[61]

$$C_6H_6 + NH_3 = H_2 + C_6H_5.NH_2.$$

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[58] SABATIER and GAUDION, *Compt. rend.*, **165**, 224 (1917).
[59] SABATIER and GAUDION, *Compt. rend.*, **165**, 310 (1917).
[60] MAILHE and DE GODON, *Compt. rend.*, **165**, 557 (1917). — MAILHE, *Ibid.*, **166**, 996 (1918).
[61] MEYER and TAUZEN, *Berichte*, **46**, 3183 (1913).

With hydrogen in presence of nickel above 350°, aniline vapors regenerate a certain amount of benzene and ammonia by the reversal of the above reaction (496).[62]

It might be hoped that the direct production of aniline from benzene vapor and ammonia would be feasible by the use of metal catalysts at 500 to 700°. It has been found that the presence of reduced *nickel, iron* or *copper* is of no advantage, as only traces of aniline are produced. Likewise only traces of *toluidine* are obtained from *toluene*. In the most favorable case working with nickeled asbestos in an iron tube, 0.11 g. aniline was obtained from 200 g. benzene.[63]

§ 7. — CLOSING OF RINGS BY LOSS OF HYDROGEN

684. Nickel. *Methyl-o.toluidine*, submitted to the action of reduced nickel at 300–30° (in presence of hydrogen), loses hydrogen to form a new cycle, yielding above 6 % of *indol* along with methane and *o.toluidine:* [64]

$$C_6H_4 \Big\langle \begin{matrix} CH_3 \\ NH.CH_3 \end{matrix} \quad \rightarrow \quad C_6H_4 \Big\langle \begin{matrix} CH \\ NH \end{matrix} \Big\rangle CH$$

Likewise *dimethyl-o.toluidine*, at 300°, yields 24 % of N-methyl-indol along with methane, toluidine and methyl-toluidine: [65]

$$C_6H_4 \Big\langle \begin{matrix} CH_3 \\ N(CH_3)_2 \end{matrix} \quad \rightarrow \quad C_6H_4 \Big\langle \begin{matrix} CH \\ N.CH_3 \end{matrix} \Big\rangle CH$$
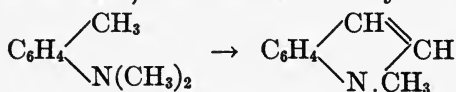
685. Aluminum Chloride. The use of *anhydrous aluminum chloride* at moderate temperatures, between 80 and 140°, causes the elimination of hydrogen with the formation of new cycles.

α-Dinaphthyl yields *perylene:* [66]

Likewise at 140°, *meso-benzo-dianthrone* passes quantitatively into *meso-naphtho-dianthrone:* [67]

[62] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 415 (1905).
[63] WIBAUT, *Berichte*, **50**, 541 (1917).
[64] CARRASCO and PADOA, *Lincei*, **15** (2), 699 (1906).
[65] CARRASCO and PADOA, *Gaz. Chim. Ital.*, **37** (2), 49 (1907).
[66] SCHOLL, SEER, and WELTZENBOCK, *Berichte*, **43**, 2203 (1910).
[67] SCHOLL and MANSFIELD, *Berichte*, **43**, 1737 (1910).

At 140° *phenyl-α-naphthyl-ketone* gives a good yield of *benzanthrone:*

This is a typical example of many analogous reactions that can be readily carried out by this process.[68]

686. **Metallic Oxides.** Various anhydrous metallic oxides, *alumina, ferric oxide, chromium trioxide, thoria,* and *titania* can cause the condensation of acetylene with various molecules with the elimination of hydrogen and the formation of cyclic compounds.

With ammonia pyrrol, picoline and collidines are formed, there being no hydrogen evolved in the formation of the latter:

$$2C_2H_2 + NH_3 = H_2 + \underline{C_4H_5N}_{\text{pyrrol}}$$

$$3C_2H_2 + NH_3 = H_2 + \underline{C_6H_7N}_{\text{picoline}}$$

$$4C_2H_2 + NH_3 = \underline{C_8H_{11}N}_{\text{collidine}}$$
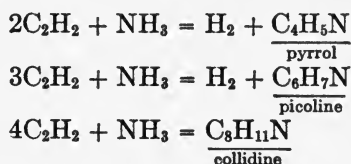
Ferric oxide is the best catalyst for forming pyrrol.

When *ethylene* is used instead of acetylene, the same products are formed but at higher temperatures and with the evolution of much hydrogen.

Hydrogen sulphide gives *thiophene:*

$$2C_2H_2 + H_2S = H_2 + C_4H_4S.$$

At 400–425°, water vapor forms *furfural:* [69]

$$2C_2H_2 + H_2O = H_2 + C_4H_4O.$$

[68] SCHOLL and SEER, *Sitz. Akad. Wien,* **120,** 11, B, 925 (1911). — ANNALEN, **394,** 111 (1912).

[69] CHICHIBABINE, *J. Russian Phys. Chem. Soc.,* **47,** 703 (1915), *C. A.,* **9,** 2512 1915).

CHAPTER XV

DEHYDRATION

687. THERE are a large number of organic reactions which take place with the elimination of water. Many of them can be started or accelerated by the presence of so-called dehydration catalysts. As might be anticipated from the great variety of reactions of this kind, dehydration catalysts comprise many substances of very different natures, elements (phosphorus, carbon, and finely divided metals), strong mineral acids (sulphuric, hydrochloric, phosphoric, etc.), either concentrated or dilute, anhydrides of acids (phosphoric and boric), anhydrous chlorides (of aluminum, zinc and iron), various inorganic salts (ammonium salts, potassium bisulphate, calcium and aluminum sulphates, phosphates, etc.), organic acids (acetic), as well as their salts (potassium and sodium acetates).

We can distinguish two distinct modes of dehydration according to whether it takes place in the gas phase by the action of solid catalysts on the vapors which are to give up the water or in the liquid medium. We will study the two separately.

§ 1. — DEHYDRATION OF ALCOHOLS ALONE

688. Primary alcohols can undergo dehydration in two different ways : to produce an ether or a hydrocarbon, usually unsaturated. Thus with ordinary alcohol, we have :

$$2CH_3.CH_2OH = H_2O + \underset{\text{ethyl ether}}{\underline{(CH_3.CH_2)_2O}}$$

and

$$CH_3.CH_2OH = H_2O + \underset{\text{ethylene}}{\underline{CH_2 : CH_2}}.$$

Benzyl alcohol gives :

$$2C_6H_5.CH_2OH = H_2O + \underset{\text{benzyl ether}}{\underline{(C_6H_5.CH_2)_2O}}$$

or

$$nC_6H_5CH_2OH = nH_2O + \underset{\text{resinous hydrocarbon}}{\underline{(C_6H_5.CH)_n}}$$
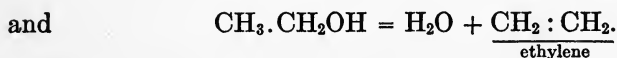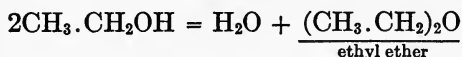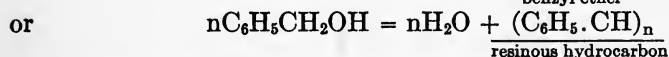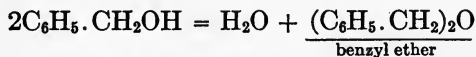
Methyl alcohol is an exception, as it can be dehydrated regularly in only one way, that is to form *methyl ether*, $(CH_3)_2O$.

Secondary alcohols, the dehydration of which is easier, yield ethers in exceptional cases only (e.g. *benzhydrol*), usually producing hydrocarbons.

The ethers can seldom be obtained from *tertiary alcohols,* as these are dehydrated to the hydrocarbons with still greater ease.

689. These dehydrations can be accomplished by a multitude of substances, that have affinity for water, used in excess compared with the alcohol that is to be dehydrated. But if the hydrates formed are unstable at the temperature of the operation, water is given off, regenerating the original substance which can repeat the reaction with a fresh quantity of alcohol.

This is what takes place with *zinc chloride* and with concentrated *sulphuric acid* of which a small quantity when heated can dehydrate a large amount of alcohol.

We have explained above (159) the mechanism of the action of *sulphuric acid* which produces either *ethyl ether* or *ethylene* from alcohol according to temperature conditions. It can continue its catalytic rôle for a long time, but is gradually diminished by being reduced to sulphur dioxide, since it slowly oxidizes the alcohol with the production of carbon dioxide and of tarry matters.

Syrupy phosphoric acid can produce an entirely analogous effect, and, as it is less readily reduced than sulphuric acid, can maintain its catalytic activity for a much longer time.[1, 2]

Formation of Ethers

690. The formation of ethers by the direct dehydration of alcohols is possible in only a small number of cases and only with primary alcohols.

In the case of *methyl alcohol* this is the only possible manner of *dehydration* and a considerable number of catalysts can decompose its vapors into *methyl ether* and water, but they are very much less numerous than the substances which can dehydrate other alcohols to hydrocarbons.

691. **Formation in Liquid Medium.** *Concentrated sulphuric acid* is usually employed to dehydrate methyl alcohol to *methyl ether.*[3]

Zinc chloride is not suitable for this reaction as it gives gaseous products by a complicated reaction and even produces a certain amount of *hexamethyl-benzene.*[4]

Ethyl ether is practically prepared by the action of *sulphuric acid* at 140°. A mixture of 5 parts of 90% *ethyl alcohol* and 9 parts of

[1] Sabatier and Mailhe, *Bull. Soc. Chim.* (4), **1,** 524, (1907).
[2] This is used for preparing ethylene on a commercial scale. — E. E. R.
[3] Dumas and Péligot, *Ann. Chim. Phys.* (2), **58,** 19 (1835).
[4] Le Bel and Greene, *Compt. rend.,* **87,** 260 (1878). — *Jahresber. Chem.,* **1878,** 388.

concentrated sulphuric acid is used. This mixture boils at about 140°. When it is heated to 140°, ether distils over and alcohol is added at such a rate that the boiling point does not rise. A large amount of alcohol can be transformed into *ether* in this way. The volume of the ether may be more than 167 times that of the sulphuric acid used.[5] Theoretically the formation should continue indefinitely, but the yield decreases after a certain time on account of the production of a carbonaceous residue which may amount to 5% of the acid and the formation of which corresponds to the evolution of a considerable amount of sulphur dioxide.

The best yield of ether is obtained between 140 and 145°, as above that temperature more and more *ethylene* is formed.[6]

Phosphoric or *arsenic acid* may replace the sulphuric acid in this preparation.[7] Anhydrous *zinc chloride* also may be used.[8]

Concentrated sulphuric acid at 135° produces *propyl ether* from the alcohol but the yield is poor because much *propylene* is formed.

The higher alcohols such as *isobutyl* do not yield ethers with concentrated sulphuric acid but only the *ethylenic hydrocarbons*.[9] Nevertheless, *isoamyl ether* can be thus obtained (696).

Sometimes sulphuric acid at 140° enables us to obtain *mixed ethers* by operating on a mixture of the two alcohols. This is the case with methyl and ethyl alcohols which yield the mixed *methyl-ethyl* ether along with the two simple ethers. In the same way *ethyl-propyl* ether may be obtained, but *ethyl-isobutyl* can not be. *Ethyl-isoamyl* ether, which several chemists have failed to obtain,[10] can be prepared along with the two simple ethers by the action of 85% sulphuric acid at 135–140°.[11]

The *mixed ethyl-tertiary-butyl ether* can be obtained by heating 50 volumes of a mixture of two molecules of ethyl alcohol and one of *trimethyl-carbinol* with one volume of sulphuric acid in a sealed tube at 100° for 5 hours.[12]

692. Although it is a secondary alcohol, *benzhydrol*, $C_6H_5.CH(OH).$-C_6H_5, is readily transformed into its ether: it is sufficient to heat it to 180° with 27% sulphuric acid.[13]

[5] Evans and Sutton, *Jour. Amer. Chem. Soc.*, **35**, 794 (1913).

[6] Norton and Prescott, *Amer. Chem. Jour.*, **6**, 243 (1884).

[7] Boulay, *Gilbert's Annalen*, **44**, 270 (1913).

[8] Masson, *Annalen*, **31**, **63**, (1839).

[9] Norton and Prescott, *Amer. Chem. Jour.*, **6**, 244 (1884).

[10] Guthrie, *Annalen*, **105**, 37 (1858). — Norton and Prescott, *Amer. Chem. Jour.*, **6**, 246 (1884).

[11] Peter, *Berichte*, **32**, 1419 (1899).

[12] Mamontoff, *J. Russian Phys. C em. Soc.*, **29**, 234 (1897), *C.*, **1897** (2), 408.

[13] Zagumenni, *J. Russian Phys. Chm. Soc.*, **12**, 431 (**1880**), *C.*, 1880, 629.

The ether may be obtained also by heating benzhydrol to 210–220° with finely divided *copper*.[14]

693. Formation in Gaseous Phase. Among anhydrous metallic oxides, only *alumina* precipitated and dried at a low temperature effects the transformation of methyl alcohol into methyl ether exclusively. The reaction commences at about 250° and is rapid at 300°, yielding methyl ether which can be completely absorbed by concentrated sulphuric acid. At about 350° the dehydration is accompanied by a slight dehydrogenation, the aldehyde produced being immediately decomposed into carbon monoxide and hydrogen.

Thoria, blue oxide of tungsten and *chromium sesquioxide* can dehydrate methyl alcohol to the ether above 230° but there is simultaneous dehydrogenation to the aldehyde and its decomposition products. The latter reaction is still more important with *titania* and takes place almost exclusively with other catalytic oxides, such as the *oxides* of *zirconium, molybdenum,* and *vanadium*.[15]

694. Alone among the oxides, *alumina* at 240° enables us to obtain *ethyl ether* from ethyl alcohol. A little *ethylene* is evolved. A 90 % alcohol may be used.

With *propyl alcohol* at 250° it gives a little *propyl ether* but forms *propylene* chiefly. It can not produce the other ethers.[16] In the apparatus of Ipatief, under high pressures, alumina can transform *ethyl alcohol* into the *ether*, but the formation is limited by the reverse reaction. At higher temperatures only ethylene is produced.[17]

Ethyl ether is totally decomposed into water and *ethylene* by *alumina* at 380°.[18]

Dehydration to Hydrocarbons

695. The dehydration of a single molecule to give a hydrocarbon with an ethylene double bond is the normal reaction of alcohols and also of *ethers*.

Reaction in Liquid Medium. This may readily be accomplished by concentrated non-volatile *mineral acids* and also by anhydrous *zinc chloride*.

696. Concentrated Mineral Acids. A small proportion of *concentrated sulphuric acid* used at a temperature high enough to eliminate the water produced serves to prepare advantageously the lower ethylenic hydrocarbons which are gases, *ethylene, propylene,* and *butylene*.

[14] KNOEVENAGEL and HECKEL, *Berichte*, **36**, 2823 (1903).

[15] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 345 (1910).

[16] SENDERENS, *Ann. Chim. Phys.* (8), **25**, 449 (1912).

[17] IPATIEF, *Berichte*, **37**, 2961 (1904).

[18] ENGELDER, *J. Phys. Chem.*, **21**, 676 (1917).

To obtain *ethylene,* a mixture of 25 parts of alcohol and 150 parts of sulphuric acid is heated to 160–70° and a mixture of alcohol and sulphuric acid is added in drops.[19]

The evolution of gas is facilitated by the addition of a certain amount of *fine quartz sand* to the mixture. According to Senderens, this acts as a true chemical catalyst. According to the same author the results are still better when 5 % of anhydrous *aluminum sulphate* is added to the usual mixture of alcohol and sulphuric acid. With *ethyl alcohol* at 157° the evolution of ethylene is thus rendered three times as rapid and *propylene* is formed at 130° instead of 145°; *isobutyl alcohol* is split at 125°.[20][21]

From 1500 cc. *isoamyl alcohol* and 100 cc. sulphuric acid in a vessel provided with a reflux condenser kept at 60–90° followed by a condenser for the amylene, 250 g. of amylene (a mixture of the 3 isomers) may be prepared in 8 hours. The alcohol remaining in the flask contains 400 g. isoamyl ether.[22]

Concentrated phosphoric acid may replace sulphuric acid in these dehydrations.

697. Under analogous conditions the dehydration of molecules with mixed function may be catalyzed. Thus *diacetonyl alcohol,* $(CH_3)_2C(OH).CH_2.CO.CH_3$, warmed with traces of sulphuric acid (6 drops to 290 g. of the alcohol), furnishes mesityl oxide, $(CH_3)_2C : CH.CO.CH_3$, with a high yield (190 g.) on distillation.[23]

698. **Zinc Chloride.** Anhydrous fused zinc chloride is very often employed to effect the transformation of alcohols into ethylene hydrocarbons, but it is commonly used in excess, that is in amount more than sufficient to fix as a stable hydrate all of the water that is eliminated. The same action can be exercised by the catalyst when the alcohol has a high boiling point as the alcohols of the *cyclohexane* series; a small quantity of the chloride serves to dehydrate these to cyclohexenes since the water that is extracted is eliminated by distillation along with the hydrocarbon so that the catalyst is continuously regenerated.

699. **Iodine.** In exceptional cases, iodine serves to effect the regu-

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[19] ERLENMEYER, *Annalen,* **192,** 244 (1878).

[20] SENDERENS, *Compt. rend.,* **151,** 392 (1910).

[21] Following the observations of SENDERENS, the following method of preparing ethylene has been devised and has given excellent service. In a 500 c.c. flask 200 c.c. conc. sulphuric acid, 100 c.c. 95 % alcohol and 25 g. of dehydrated alum are heated to 157 to 175°, the thermometer dipping in the mixture. One operator repeated this five times in an afternoon and obtained 667 g. ethylene bromide. —E. E. R.

[22] ADAMS, KAMM, and MARVEL, *Jour. Amer. Chem. Soc.,* **40,** 1950 (1918).

[23] KOHN, *Monatsh. Chem.,* **34,** 779 (1913).

lar dehydration of compounds containing alcohol groups. *Diacetonyl alcohol*, $(CH_3)_2C(OH).CH_2.CO.CH_3$, which distillation alone breaks down partially into two molecules of acetone, is dehydrated by sulphuric acid to *mesityl oxide* (697). The same dehydration takes place quantitatively when it is distilled with a small amount of iodine.[24]

700. Reaction in Gaseous System. This can be effected by a large number of solid catalysts among which the best are *alumina, clay, thoria* and the *blue oxide of tungsten*.

Elements. *Animal charcoal*, extracted with hydrochloric acid, is a rather mediocre catalyst for alcohols : above 350° it produces ethylene from *ethyl alcohol*, accompanied by a certain amount of methane, carbon monoxide and hydrogen resulting from the formation of acetaldehyde which is mostly destroyed. Propyl alcohol, above 300°, gives a gas of which 87 % is propylene, with ethylene and other gaseous products.[25]

Red phosphorus acts more rapidly at much lower temperatures and probably owes this activity to small amounts of phosphorus and phosphoric acids preëxistent in the material and which are formed in considerable amounts in consequence of the oxidation of the phosphorus by the alcohol with a correlative production of phosphine.

With *ethyl alcohol* at 240°, a rapid evolution of ethylene is obtained containing 5 % phosphine. Similar results are obtained with *propyl alcohol*. The proportion of phosphine is less with *normal* and *iso-butyl alcohols* and negligible with *isopropyl alcohol* which is already split at 150°.

The presence of phosphine, which is difficult to get rid of, takes away much of the interest in this case of catalysis.

701. Finely *divided metals* have an important catalytic dehydrogenating effect on primary and secondary alcohols (651); but they decompose *tertiary* alcohols rapidly at moderate temperatures into unsaturated hydrocarbons. *Reduced nickel* acts in this way without complications at 220 to 300° and *reduced copper* acts similarly above 280 to 300°.[26]

Passing an aliphatic alcohol over copper at 300° is a simple method of determining its class. A primary alcohol forms an aldehyde, a secondary one a ketone, while a tertiary breaks up into water and an unsaturated hydrocarbon.[27]

702. Anhydrous Metal Oxides. Grigoreff in 1901 was the first to note the special aptitude of an *oxide* to dehydrate alcohols : he found

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[24] HIBBERT, *Jour. Amer. Chem. Soc.*, **37**, 1748 (1915).

[25] SENDERENS, *Compt. rend.*, **144**, 381 (1907).

[26] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 467 and 472 (1905).

[27] SABATIER and SENDERENS, *Bull. Soc. Chim.* (3), **33**, 263 (1905).

that *alumina* decomposes ethyl and propyl alcohols to the hydrocarbons with 90 % yields.[28]

This property of *alumina* was studied by Ipatief and found also in the material of graphite crucibles, which is a mixture of graphite (inactive) and *clay*, while other oxides (of zinc, iron, tin, chromium, etc.) were revealed as dehydrogenating catalysts.[29]

The catalytic activity of various oxides was made the object of a thorough study by Sabatier and Mailhe,[30] who were able to demonstrate the great dehydrating power of *thoria* and of the *blue oxide of tungsten*. We have already noted (675) that the oxides that are not reducible, or only slowly reducible, by alcohols can be divided into *dehydrogenating*, *dehydrating*, and mixed catalysts which cause both reactions simultaneously.

The direction and the importance of the activity of the various oxides can be clearly shown by a comparison of the volume and composition of the gas evolved by them, when equal volumes of them are used at 340–50° with the same amount of ethyl alcohol; all of the oxides having been prepared below 350°:[31]

	Oxide	Volume of gas in cc. per min.	Composition C_2H_4 %	H_2 %
Dehydrating	ThO_2	31	100	trace
	Al_2O_3	21	98.5	1.5
	W_2O_5	57	98.5	1.5
Mixed	Cr_2O_3	4.2	91	9
	SiO_2	0.9	84	16
	TiO_2	7.0	63	37
	BeO	1.0	45	55
	ZrO_2	1.0	45	55
	UO_2	14	24	76
	Mo_2O_5	5	23	77
	Fe_2O_3	32	14	86
	V_2O_3	14	9	91
	ZnO	6	5	95
Dehydrogenating	MnO	3.5	0	100
	MgO	traces	0	100

[28] Grigoreff, *J. Russian Phys. Chem. Soc.*, **33**, 173 (1901).

[29] Ipatief, *Berichte*, **34**, 596 (1901); **35**, 1047 (1902); **36**, 1990 (1903).

[30] Sabatier and Mailhe, *Bull. Soc. Chim.* (4), **1**, 107, 341, 524 and 733 (1907). — *Compt. rend.*, **146**, 1376 (1908); **147**, 16 and 106 (1908); **148**, 1734 (1909). — *Ann. Chim. Phys.* (8), **20**, 289 (1910).

[31] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **20**, 341 (1910).

703. We have noted (76) that the *physical condition* and the method of preparation of an oxide have a great influence on its activity and even on the direction of the catalysis.

These differences are very marked for the various varieties of *chromium sesquioxide* (78) the only one of which that is suitable for the dehydration of alcohols is that obtained by drying the precipitated blue hydrated hydroxide below 350°.

704. **Titanium oxide,** TiO_2, prepared by calcining at a red heat has very little activity. To obtain a suitable oxide, the hydroxide prepared by the action of ammonia on titanium chloride is dehydrated below 350°.[32]

705. **Crystallized silica** is almost without action on alcohols below 400°. The pure silica obtained by decomposing silicon fluoride by water, washing thoroughly and drying at 300°, is also only slightly active. The most active form is obtained by adding dilute acid to *sodium silicate,* washing and drying the gelatinous precipitate.

706. The most active form of *alumina* is prepared by precipitation from aluminum nitrate, washing the precipitate well and drying at 300°. Good results are also obtained with the oxide prepared by calcining pure *ammonium alum* at red heat. The *basic aluminum sulphate* obtained by calcining aluminum sulphate at a dull red is a very active catalyst. On the contrary, preparations of alumina which have been heated to redness for a long time are almost inactive and sometimes do not give an appreciable amount of gas from ethyl alcohol even at 420°.[33]

Bauxite, aluminum hydroxide mingled with silica and ferric hydroxide, has low catalytic power and dehydrogenates chiefly at about 400°.[34]

The nature of the reaction catalyzed is closely connected with the condition of the oxide and bears a certain relation to its ease of solution in acids.[35]

707. **Thoria,** on the contrary, does not present these difficulties and its catalytic activity is not sensibly diminished by calcination at

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[32] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 325 (1910).

[33] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 300 (1910).

[34] Samples of bauxite from different sources differ widely in catalytic power. With isoamyl alcohol a sample of German bauxite gave gaseous products but poor yields of amylene, while a Tennessee sample gave little gas and an excellent yield of amylene. The bauxite was used in a copper tube 35 x 900 mm. at about 400°, the alcohol being admitted at about 100 drops per minute. Several pounds of amylene were thus prepared. — C. H. Milligan.

[35] IPATIEF, *Berichte,* **37,** 2986 (1904).

red heat : it seems that its high molecular weight may be in the way of molecular condensations such as alumina appears to undergo when heated to redness.[36]

708. There are great differences in the *duration* of the catalytic activity of various oxides; usually it goes on decreasing because the surface of the oxide is gradually covered by small amounts of tarry or carbonaceous matter which hinder gaseous exchanges and also because molecular condensations take place in the oxides, without doubt, even when the temperature of the reaction is below 400°. If we consider only the three good dehydration catalysts, alumina, thoria, and the blue oxide of tungsten, alumina, the lightest molecule (Al_2O_3, molecular weight 92) is the one which weakens most rapidly. An active specimen which disengaged 14 cc. ethylene per minute at 340°, gave only 7 cc. after three hours of use.[37]

However certain observers have found no weakening after five hours.[38] [39]

The *blue oxide of tungsten* is much more permanent : the evolution of gas may continue for several hours without noticeable weakening. The same is true of *thoria* which has the great additional advantage of being very readily regenerated when long usage has gummed it up; calcining at a red heat for a few instants is sufficient to render it perfectly white and restore its original activity.[40]

709. For a given catalyst, elevating the *temperature* greatly accelerates the reaction. By operating under the same conditions with ethyl alcohol and the blue oxide of tungsten, it has been found that the evolution of *ethylene* begins at about 250° and becomes more and more rapid as the temperature rises. The yield per minute was :

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[36] In the catalytic preparation of mercaptans, KRAMER and REID (*J. Amer. Chem. Soc.* **43**, 882 (1921)) find that the activity of a thoria catalyst depends somewhat on the temperature to which it has been subjected, being considerably diminished by heating much above 400°. Some preparations of thoria such as Welsbach gas mantles and the extremely voluminous product obtained by dropping thorium nitrate into a red hot crucible are absolutely inactive so far as this reaction is concerned. — E. E. R.

[37] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 299 (1910).

[38] ENGELDER, *J. Phys. Chem.*, **21**, 676 (1917).

[39] I have used the same alumina catalyst for many days in making ethylene without noticing any deterioration. — E. E. R.

[40] A thoria catalyst may be cleaned by passing steam over it at 380° till all volatile material is removed and following this with nitrogen peroxide at the same temperature as long as there is any action, the oxides of nitrogen being finally displaced by steam. A catalyst so regenerated is snow white and shows its original activity. — KRAMER and REID, *J. Amer. Chem. Soc.* **43**, 884 (1921).

Temperature	C.c. per minute
260°	5
300°	17.5
310°	27
330°	48.5
340°	57.5
370°	73

But it must be remembered that for any given oxide, the elevation of the temperature tends to introduce and make more and more prominent the reaction of dehydrogenation. Thus at 340° *titania* produces practically pure ethylene from alcohol, but at 340° with a more rapid evolution of gas there is some hydrogen, while at 360° the hydrogen amounts to one third of the gas.[41]

Above 400° the gas produced may contain *ethane* along with the hydrogen.[42]

710. The presence of water in the alcohol is unfavorable to dehydration but does not interfere with dehydrogenation. Thus with alcohol diluted with its own volume of water, alumina gives a gas containing twice as much hydrogen as with absolute alcohol.[42]

711. Increase of *pressure* retards the dehydration of alcohols, or rather raises the temperature at which this takes place; the intermediate production of the ether from primary alcohols is favored by increase of pressure which is unfavorable to the separation of the hydrocarbon.[43]

712. The dehydration of alcohols higher than propyl, effected by oxides or by other catalysts, usually leads to the production of several *isomeric* unsaturated hydrocarbons and frequently also to the formation of a certain proportion of *polymers* (211).

713. **Alumina.** The best results are obtained with alumina precipitated from aluminum nitrate by ammonia, well washed and dried at 300°.

The dehydration of *methyl* alcohol begins at about 250° and is rapid below 300°, yielding exclusively methyl ether absorbable by concentrated sulphuric acid. At about 350°, the ether is accompanied by a small amount of aldehyde, a little of which is condensed, and hydrogen is collected containing carbon monoxide resulting from the partial decomposition of the formaldehyde.

With *ethyl* alcohol, ether is formed above 240° and at 290° pure *ethylene* is evolved regularly, this evolution becoming rapid at 340°.

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[41] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 325 (1910).

[42] ENGELDER, *J. Phys. Chem.*, **21**, 676 (1917).

[43] IPATIEF, *J. Russian Phys. Chem. Soc.*, **36**, 786 and 813 (1904), *C.*, **1904** (2), 1020 and **38**, 63 and 92 (1906), *C.*, **1906** (2), 86 and 87.

It is not necessary to go beyond 360° where the ethylene begins to be decomposed and where its evolution slows down rather rapidly on account of the weakening of the catalyst.[44]

Propyl alcohol gives a regular current of propylene above 300° without any of the ether.

Normal and *iso-butyl* alcohols likewise give a regular evolution of hydrocarbons entirely absorbable by sulphuric acid. Both yield mixtures of the isomeric hydrocarbons, C_4H_8.[45] However, Ipatief obtained pure isobutylene from isobutyl alcohol.[46]

With *isoamyl* alcohol, the dehydration goes readily, the best yield being obtained between 500 and 540°. The product contains several isomeric hydrocarbons, C_5H_{10}, but the proportion of *isopropyl-ethylene* is greater than in the dehydration by sulphuric acid.[47]

At 450°, *secondary butyl* alcohol gives pure butylene and *tertiary* butyl alcohol, or *trimethyl-carbinol*, yields only isobutylene.[48]

At a dull red, *allyl alcohol* evolves quite pure *propylene* with a correlative production of *acroleïne*.[49]

714. Benzyl alcohol is readily dehydrated at above 300° to form the yellowish resinous hydrocarbon $(C_7H_6)_x$, without evolution of gas.[50]

Other primary, secondary, or tertiary aromatic alcohols are readily dehydrated by alumina without complications below 350°, with the production of the corresponding unsaturated hydrocarbons. Thus *phenyl-benzyl-carbinol*, $C_6H_5.CH(OH).CH_2.C_6H_5$, yields *stilbene*, $C_6H_5.-CH:CH.C_6H_5$, quantitatively.[51]

Borneol gives *menthene* and the various secondary or tertiary *cyclohexyl alcohols* are readily changed to the corresponding *cyclohexene* hydrocarbons. Thus *cyclohexanol* is entirely transformed into *cyclohexene* and *1.2-dimethyl-cyclohexanol* yields *1.2-dimethyl-cyclohexene*.[52]

At 350° and 30 to 40 atmospheres with alumina, *decahydronaphthol* yields *octahydronaphthalene*, $C_{10}H_{16}$, boiling at 197°.[53]

715. **Blue Oxide of Tungsten.** *Tungstic oxide* is readily reduced by alcohol vapors above 250° and brought to the *blue oxide*, intermediate between WO_3 and WO_2, approaching the composition W_2O_5

[44] Sprent, *J. Soc. Chem. Ind.*, **32**, 171 (1913).

[45] Senderens, *Bull. Soc. Chim.* (4), **1**, 692 (1907).

[46] Ipatief and Sdzitowecky, *Berichte*, **40**, 1827 (1907).

[47] Adams, Kamm and Marvel, *J. Amer. Chem. Soc.*, **40**, 1950 (1918).

[48] Ipatief and Sdzitowecky, *Berichte*, **40**, 1827 (1907).

[49] Krestinsky and Nikitine, *J. Russian Phys. Chem. Soc.*, **44**, 471 (1912).

[50] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **20**, 298 (1910).

[51] Sabatier and Murat, *Ann. Chim.* (9), **4**, 284 (1915).

[52] Ipatief and Rutala, *J. Russian Phys. Chem. Soc.*, **44**, 1692 (1912).

[53] Ipatief, *Berichte*, **43**, 3383 (1910).

more and more nearly, and which on exposure to the air, after cooling, reoxidizes spontaneously, more or less rapidly regenerating the original yellow oxide.

This blue oxide is a mediocre catalyst for *methyl* alcohol which it does not attack till 330°, dehydrating and dehydrogenating it simultaneously, but is an excellent dehydration catalyst, very active and very regular, for other alcohols.[54] By using a train of blue tungsten oxide 51 cm. long at 340° and vaporizing 17 g. of alcohol per hour a regular evolution of 101 cc. ethylene per minute containing only 1 or 2 % of hydrogen, was obtained, 5.1 g. of the alcohol escaping decomposition. By doubling the rate of flow of the alcohol the evolution of gas reached 140 cc. per minute.

At 320°, *propyl, isobutyl* and *isoamyl alcohols* give good yields of the unsaturated hydrocarbons, and *benzyl alcohol* is rapidly transformed into crusts of the yellow polymer (714).

716. **Thoria.** For all the alcohols, except methyl, thoria is a very regular catalyst, the properties of which have already been mentioned (708).

With *ethyl* alcohol, the reaction begins around 280° and is readily accelerated by rise of temperature. By using a boat containing 4.7 g. thoria, at 325°, 11 cc., and at 350°, 31 cc. of practically pure ethylene were obtained per minute.

The results are equally good with *propyl* and *isobutyl* alcohols and with the other alcohols mentioned under alumina.

The secondary alcohol, *isopropyl*, begins to yield propylene at 260°.

717. **Mineral Salts.** *Clay,* or *hydrated aluminum silicate,* and particularly the white variety, *kaolin,* has a remarkable dehydrating power with alcohols.[55]

The fragments of a *graphite* crucible (a mixture of graphite and clay) gave Ipatief a good yield of unsaturated hydrocarbons from alcohols.[56]

In 1906, Bouveault noted the special activity of clay and designed an apparatus for using it for the dehydration of various alcohols quite similar to that which he employed for their dehydrogenation over copper (654). The catalyst consisted of clay balls about 1 cc. in volume, dried at 300° in a current of air and packed in the 1 m. vertical tube of the apparatus in which about 1 k. of alcohol per day could be dehydrated. *Ethyl, propyl, isobutyl* and *cyclohexyl alcohols*

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[54] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 328 (1910).

[55] Kaolin was used as catalyst in preparation of ethylene at Edgwood Arsenal, U. S. A., during the war. — E. E. R.

[56] IPATIEF, *Berichte,* **36**, 1990 (1903).

are readily dehydrated by this means. In the case of *isoamyl alcohol* the hydrocarbons are isomerized as with alumina or zinc chloride.[57]

All *aluminum* salts have more or less of the catalytic power of alumina. The basic aluminum sulphates obtained by calcining neutral aluminum sulphate at a dull red [58] and likewise the mixtures of these with alkali sulphates obtained by calcining potassium and sodium alums have this power.

718. **Calcium sulphate** is a mediocre catalyst. When obtained by calcining gypsum at a moderate temperature, it gives with alcohol at 420° an evolution of ethylene containing 6 % of hydrogen, while if it is prepared at a red heat, it gives a very slow evolution of hydrogen containing 14 % of ethylene at 460°.[59]

719. **Aluminum phosphate** is recommended as a good catalyst by Senderens, who explains this aptitude as a sort of culmination of the catalytic power of alumina and that of phosphorus.[60] *Ethyl alcohol* is decomposed above 330° and rapidly at 380°. With *propyl*, dehydration commences at 300° and is rapid at 340°; with *butyl*, the reaction is important at 320°. *Isoamyl alcohol* is attacked at above 300°, while 250° is high enough to decompose isopropyl, which goes rapidly at 300°. The decomposition of *trimethyl-carbinol* begins at 140°.[61]

720. **The Case of Benzhydrol.** We have noted above (692), that benzhydrol, $C_6H_5 \cdot CH(OH) \cdot C_6H_5$, heated to 210° with copper powder gives the ether, $((C_6H_5)_2CH)_2O$, in 75 % yield instead of *benzophenone*. At a higher temperature, 290°, copper powder produces benzophenone chiefly with a slow evolution of hydrogen, along with a little of the ether and of *diphenylmethane*.[62]

In fact the alcohol is dehydrogenated to benzophenone but the liberated hydrogen is used for the most part immediately to form diphenylmethane and particularly symmetrical tetraphenyl-ethane :

$$C_6H_5 \cdot CH(OH) \cdot C_6H_5 = H_2 + C_6H_5 \cdot CO \cdot C_6H_5$$
$$C_6H_5 \cdot CO \cdot C_6H_5 + 2H_2 = H_2O + C_6H_5 \cdot CH_2 \cdot C_6H_5$$
$$2C_6H_5 \cdot CO \cdot C_6H_5 + 3H_2 = 2H_2O + (C_6H_5)_2CH \cdot CH(C_6H_5)_2$$
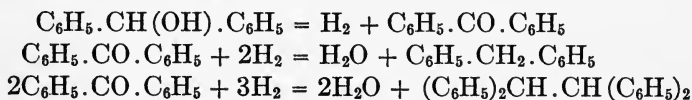
Dehydrating catalysts lead to the same result as copper. The vapors of benzhydrol passed over thoria at 420° give, *without elimination of hydrogen*, a mixture of benzophenone, diphenylmethane and *sym*.tetraphenyl-ethane with the separation of water simply.[63]

[57] Bouveault, *Bull. Soc. Chim.* (4), **3**, 117 (1908).

[58] Sabatier and Mailhe, *Ann. Chim. Phys.* (8), **20**, 300 (1910).

[59] Senderens, *Bull. Soc. Chim.* (4), **3**, 633 (1908).

[60] Senderens, *Bull. Soc. Chim.* (4), **1**, 690 (1907).

[61] Senderens, *Compt. rend.*, **144**, 1109 (1907).

[62] Knoevenagel and Heckel, *Berichte*, **36**, 2816 (1903).

[63] Sabatier and Murat, *Ann. Chim.* (9), **4**, 282 (1915).

721. Catalytic Passage from an Alcohol to the Corresponding Hydrocarbon. This passage is realized easily in two successive steps : 1st dehydration of the alcohol over alumina or thoria to the unsaturated hydrocarbon; 2nd hydrogenation of this hydrocarbon over a slightly active nickel at 200–50° :

$$\underset{\text{alcohol}}{\underline{C_nH_{2n+1}OH}} = C_nH_{2n} + H_2O$$
$$C_nH_{2n} + H_2 = C_nH_{2n+2}$$
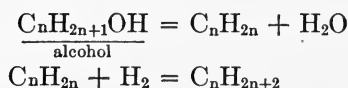
A large number of syntheses of hydrocarbons in this way have been reported by Sabatier and Murat; for example, *uns.diphenyl-ethane* $(C_6H_5)_2CH.CH_3$ was prepared from *methyl-diphenyl-carbinol*, $(C_6H_5)_2$-$C(OH).CH_3$.[64]

722. The two reactions can be superimposed by submitting the alcohols to the simultaneous action of alumina and nickel, but a necessary condition is that the two reactions can be carried on at the same temperature which is usually impracticable at the ordinary pressure. They can be readily carried on simultaneously in the apparatus of Ipatief (585). Thus *fenchyl alcohol* (40 g.) with alumina (1.5 g.) and nickel oxide (2.5 g.) with hydrogen at 110 atmospheres for 40 hours at 230° gave a good yield of *fenchane*, boiling at 162°, and *carvomenthol* gave *menthane*.

Camphor, when treated under the same conditions at 220°, is changed into *isocamphene*, melting at 63°. The succession is doubtless :[65]

$$\underset{\text{camphor}}{\underline{C_{10}H_{16}O}} \longrightarrow \underset{\text{borneol}}{\underline{C_{10}H_{18}O}} \longrightarrow \underset{\text{camphene}}{\underline{C_{10}H_{16}}} \longrightarrow \underset{\text{camphane}}{\underline{C_{10}H_{18}.}}$$

Catalytic Dehydration of Poly-alcohols

723. It is seldom that the dehydration of poly-alcohols leads to hydrocarbons; aldehydes and ketones are commonly formed.

However, it has been found that when the vapors of *2-methyl-butane-diol(1.3)* are passed over *kaolin* at above 400°, *isoprene* is formed :[66]

$$HOCH_2.CH(CH_3).CH(OH).CH_3 = 2H_2O + CH_2:C(CH_3).CH:CH_2.$$
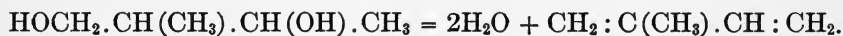
Quinite, $C_6H_{10}(OH)_2$, submitted to the action of alumina at 350° and 30 to 40 atmospheres pressure, is dehydrated to *dihydro-benzene*,

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[64] SABATIER and MURAT, *Ann. Chim.* (9), **4**, 254 (1915).
[65] IPATIEF and MATOW, *Berichte*, **45**, 3205 (1912).
[66] KYRIAKIDES and EARLE, *U. S. Patents*, 1,094,222, 1,094,223 and 1,106,290.

C_6H_8, along with some *tetrahydro-phenol*, $C_6H_9.OH$, resulting from the incomplete dehydration.[67]

724. Glycol, $HOCH_2.CH_2OH$, heated at 400° with *alumina* yields chiefly *acetaldehyde* which condenses partially to *paraldehyde*.

Pinacone, $(CH_3)_2C(OH).C(OH)(CH_3)_2$, is changed at 300–20° into *pinacoline* as it is by the action of dilute sulphuric acid.[68]

725. Glycerine in the liquid form to which are added small amounts of alumina, aluminum sulphate or potassium bisulphate, is dehydrated to acroleïne at about 110°:

$$HOCH_2.CH(OH).CH_2OH = 2H_2O + CH_2:CH.CHO.$$
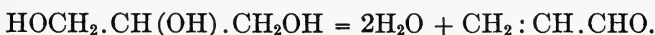
To 100 parts of glycerine, 4 parts anhydrous aluminum sulphate, 8 parts of the hydrated, or 5 of potassium bisulphate are used. The yield is 17 to 19%, or a little smaller than when 227 parts of bisulphate are used as in the ordinary method.[69]

This process has the inconvenience that acetaldehyde and sulphur dioxide are evolved; the same is true when these catalysts are replaced by *ferric* or *cupric sulphates*.

Better results are obtained with anhydrous *magnesium sulphate*, with which more than 50% of the theoretical yield is obtained at 330–40°, with negligible amounts of by-products, while at 360° acetaldehyde appears.[70]

726. Dehydration in the Gaseous Phase. When the vapors of glycerine are passed over *alumina* at about 360°, complete dehydration to *acroleïne* takes place, but a portion of this is decomposed into *ethylene* and *carbon monoxide* while another portion is crotonized to higher aldehydes which condense along with the water and acroleïne.[71]

When for the *alumina* catalyst is substituted *black uranous oxide*, which dehydrates and dehydrogenates alcohols at the same time, with a predominance of the latter reaction (675), results intermediate between those with alumina and those with copper (680) are obtained.

By using *kaolin* at 380–400° or *aluminum phosphate* at 450° we can transform *butane-diol* (*1.3*) into *butadiene* regularly or *pentane-diol-* (*2.4*) into *piperylene*. The presence of a little *hydrobromic acid* or of aniline hydrobromide increases the yield which for piperylene reaches 50%.

[67] IPATIEF, *Berichte*, **43**, 3383 (1901). — *J. Russian Phys. Chem. Soc.*, **42**, 1552 (1911).

[68] IPATIEF, *J. Russian Phys. Chem. Soc.*, **38**, 92 (1906).

[69] SENDERENS, *Bull. Soc. Chim.* (4), **3**, 828 (1908). — *Compt. rend.*, **151**, 530 (1910).

[70] WOHL and MYLO, *Berichte*, **45**, 2046 (1912). — WITZEMANN, *J. Amer. Chem. Soc.*, **36**, 1766 (1914).

[71] SABATIER and GAUDION, *Compt. rend.* **166**, 1034 (1918).

Pinacone is likewise dehydrated to *dimethyl-butadiene* when its vapors are passed over copper at 430–500° and the yield is raised to 70 % by the presence of a little hydrobromic acid.[72]

727. Ring Formation by the Dehydration of Poly-alcohols. Long chain molecules containing several alcohol groups can pass into the *furfurane* ring by catalytic dehydration in solution.

Arabinose, $HOCH_2.CH(OH).CH(OH).CH(OH).CHO$, when boiled with sulphuric acid diluted to one third, is converted into *furfural,*[73]

$$
\begin{array}{c}
\text{CH}\!\!-\!\!\text{CH} \\
\ \| \qquad \| \\
\text{CH} \quad \text{C}-\text{CHO} \\
\diagdown \text{O} \diagup
\end{array}
$$
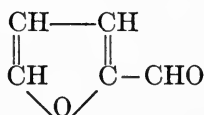
Mucic acid or *saccharic acid,* $HOOC.(CHOH)_4.COOH$, heated to 100° with hydrochloric acid, loses two molecules of water to form *dehydro-mucic* or *furfurane-dicarbonic acid* :[74]

$$
\begin{array}{c}
\text{CH}\!\!-\!\!\text{CH} \\
\ \| \qquad \| \\
\text{C} \qquad \text{C} \\
\text{HOOC}\diagup \ \diagdown \text{O} \diagup \ \diagdown\text{COOH}
\end{array}
$$
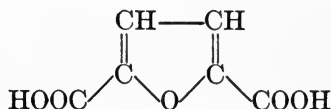
[72] Kyriakides, *J. Amer. Chem. Soc.,* **36,** 980 (1914).
[73] Stone and Tollens, *Annalen,* **249,** 237 (1888).
[74] Yoder and Tollens, *Berichte,* **34,** 3446 (1901).

CHAPTER XVI

DEHYDRATION (Continued)

§ 2. — ELIMINATION OF WATER BETWEEN AN ALCOHOL AND A HYDROCARBON

728. THE use of *anhydrous aluminum chloride* enables us to condense an *aromatic alcohol* with an *aromatic hydrocarbon* in the liquid phase. Thus *benzyl alcohol*, $C_6H_5.CH_2OH$, and *benzene* give *diphenyl-methane*, $C_6H_5.CH_2.C_6H_5$, accompanied by a certain amount of *ortho* and *para dibenzyl-benzenes* and other hydrocarbons among which is found *anthracene*.[1] The same reaction takes place with *secondary aromatic alcohols* which yield *tertiary* hydrocarbons. With benzene we have :

$$C_6H_5.CH(OH).R + C_6H_6 = H_2O + C_6H_5.CH{\overset{\displaystyle R}{\underset{\displaystyle C_6H_5}{<}}}.$$
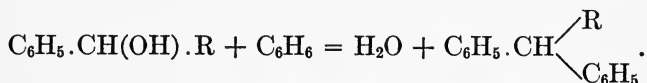
The yield is better when R is an aromatic residue than when it is *methyl* or specially *ethyl*. The use of an excessive quantity of aluminum chloride, particularly if the temperature is high, may lead to the elimination of a phenyl group or of an aliphatic residue, R.[2]

By adding aluminum chloride to a mixture of *methyl-phenyl-carbinol*, $C_6H_5.CH(OH).CH_3$, and benzene kept at 25–35°, a 20 % yield of *diphenyl-ethane* is obtained along with *ethyl-benzene*, *diphenyl-methane*, and *anthracene*, due to a further action of the chloride. By operating at 10° with 5 molecules of benzene and 0.5 of aluminum chloride a 65 % yield of *diphenyl-ethane* is obtained.

Under the same conditions, *ethyl-phenyl-carbinol* forms diphenyl-propane in 40 % yield.

Benzhydrol dissolved in 5 molecules of benzene to which is added 1 molecule of aluminum chloride at 35–40°, gives a 40 % yield of *triphenyl-methane* with some *diphenyl-methane*. By operating below 10°, the yield of triphenyl-methane reaches 65 to 70 %.[3]

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[1] HUSTON and FRIEDEMANN, *J. Amer. Chem. Soc.*, **38**, 2527 (1916).

[2] HUSTON and FRIEDEMANN, *J. Amer. Chem. Soc.*, **40**, 785 (1918).

[3] HUSTON and FRIEDEMANN, *J. Amer. Chem. Soc.*, **40**, 785 (1918).

§ 3. — ELIMINATION OF WATER BETWEEN AN ALCOHOL AND AMMONIA OR AMINES

Reactions in Liquid Systems

729. The *primary aliphatic alcohols* heated for several hours at 220° in an autoclave with *aniline* and a very small amount of *iodine* as a catalyst, give good yields of the corresponding *alkyl-anilines.*[4]

Thus by heating equal molecules of aniline and *methyl alcohol* for 9 hours at 230° with 1 % of iodine, a yield of 73 % of *methyl-aniline* is obtained. By using 2 molecules of the *methyl alcohol*, 86 % of *dimethyl-aniline* is obtained in 7 hours under the same conditions.

By heating 1 molecule of aniline and 4 molecules of ethyl alcohol with 0.5 g. iodine 10 hours, 95 % of *diethyl-aniline* is obtained.

Under the same conditions, *benzyl alcohol* and *aniline* give *benzyl-* or *dibenzyl-aniline* and *isoamyl alcohol* furnishes *amyl-* and *diamyl-anilines.*

With alcohols and a little iodine, α- and β-*naphthyl-amines* react similarly.

730. **Aromatic Alcohols** may condense with *aniline* or its homologs when they are heated gently with *dilute hydrochloric acid.*[5] Thus *tetra-methyl-diamino-benzhydrol*, $(CH_3)_2N . C_6H_4 . CH (OH) . C_6H_4 . N (CH_3)_2$, eliminates a molecule of water with aniline to give *tetramethyl-leucaniline*, $((CH_3)_2N . C_6H_4)_2CH . C_6H_4 . NH_2$.

Reactions in Gaseous Systems

731. We have seen above that the catalytic dehydration of alcohols by various anhydrous metallic oxides has been explained by Sabatier and Mailhe on the assumption of the formation of a sort of unstable *ester* between the alcohol and the oxide acting as an acid, *e.g.* an alcohol *thorinate* (603).

But according to the fundamental method of Hofmann, ammonia acts on the esters of mineral acids to form amines. Sabatier and Mailhe have imagined that the unstable esters formed with the oxides should behave in the same way. It was to be hoped that, at least for some oxides, the reaction of ammonia with the temporary ester should be more rapid than the decomposition of this ester into an ethylenic hydrocarbon.[6]

[4] KNOEVENAGEL, *J. prakt. Chem.* (2), **89**, 30 (1914).
[5] BADISCHE, *German Patent*, 27,032 (1883).
[6] SABATIER and MAILHE, *Compt. rend.*, **150**, 823 (1910).

Experiment has fully verified this expectation. Thus with thoria and an aliphatic alcohol we have :

$$2C_nH_{2n+1}.OH + ThO_2 = H_2O + \underset{\text{thorinate}}{\underline{ThO(OC_nH_{2n+1})_2}}$$

Then :

$$ThO(OC_nH_{2n+1})_2 + 2NH_3 = H_2O + \underset{\text{amine}}{\underline{HC_nH_{2n+1}.NH_2}} + \underset{\text{regenerated}}{\underline{ThO_2}}$$
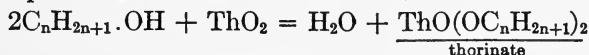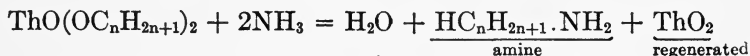
a succession of reactions which is equivalent to the single reaction :

$$C_nH_{2n+1}.OH + NH_3 = H_2O + \underset{\text{amine}}{\underline{C_nH_{2n+1}.NH_2}}.$$
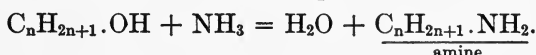
732. This reaction does not take place in the absence of a catalyst, but does go well in the presence of thoria at 300–50°, the dehydration into an unsaturated hydrocarbon being only a side reaction. Thus with *ethyl alcohol*, which is largely broken down to ethylene by thoria at 350°, the presence of ammonia almost completely prevents the evolution of the hydrocarbon but causes the production of *ethyl-amine*. The same is true with other dehydrating catalysts, *alumina, blue oxide of tungsten* and equally with the mixed catalysts, such as *titania, chromic oxide, blue oxide of molybdenum, zirconia*, etc. The formation of the amine directs the activity of the catalysts to its profit : the decomposition of alcohols into aldehydes and hydrogen as well as into water and ethylenic hydrocarbons is almost suppressed and the formation of the amine predominates.

Furthermore the *primary amine* thus produced reacts in its turn on the alcohol in the presence of the catalytic oxide as does ammonia, and forms the *secondary amine:*

$$C_nH_{2n+1}.OH + C_nH_{2n+1}.NH_2 = H_2O + (C_nH_{2n+1})_2NH$$

and there is the possibility of the formation of some tertiary amine by the action of the secondary on the alcohol.

733. The direct action of ammonia gas on alcohols is a *general method for the preparation of amines*. Into a tube containing several grams of thoria heated below 350° (from 250 to 350° according to circumstances) are passed at the same time alcohol vapors and ammonia (furnished very conveniently by a cylinder of liquid ammonia). The liquid condensed at the other end of the tube is a mixture of ammoniacal water, primary and secondary amines (with traces of tertiary) and untransformed alcohol holding in solution a certain amount of the ethylenic hydrocarbon. The latter products are easily separated from the amines by fractional distillation.[7]

From propyl alcohol, *mono-* and *dipropyl-amines* can be readily prepared and *mono-* and *di-isoamyl-amines* from isoamyl alcohol.

[7] SABATIER and MAILHE, *Compt. rend.*, **148**, 898 (1909).

734. Likewise *benzyl alcohol* and ammonia with thoria at 300–350° give only a small amount of the resinous hydrocarbon $(C_7H_6)_x$, but yield chiefly *benzyl-* and *dibenzyl-amines*, and a small amount of *tribenzyl-amine*, which solidifies in the condenser tube. By operating at 330°, benzyl-amine is the main product, while at 370–380°, dibenzyl-amine predominates, but there is at this temperature a notable decomposition of the alcohol to the aldehyde, which, in turn, is split into benzene and carbon monoxide.[8]

735. The secondary alcohol, *isopropyl*, does not suffer appreciable dehydration over thoria at 250°, but at that temperature ammonia is effective and gives about 20 % of *isopropyl-amine* accompanied by a little *di-isopropyl-amine*. Around 300° a considerable evolution of propylene is observed and the condensed liquid contains about one third isopropyl-amine and about the same amount of secondary, along with water and unchanged alcohol.[9]

Likewise *diethyl-carbinol* and *dipropyl-carbinol* give mixtures of the corresponding primary and secondary amines.[10]

736. The method is less easy to apply to *benzhydrol:* yet its vapors when carried by an excess of ammonia over thoria at 280° give some *benzhydryl-amine*, but dehydration preponderates producing *tetraphenyl-ethylene*.

737. The secondary *cyclohexane* alcohols (cyclohexanol and its homologs) are dehydrated rapidly in contact with thoria at 300–350° but in the presence of ammonia at 290–320° the reaction is, for the most part, directed toward the formation of amines, hardly more than 30 to 40 % of the unsaturated hydrocarbons being simultaneously produced.

In this way *cyclohexyl-amine* and the three *methyl-cyclohexyl-amines* have been prepared, some of the secondary amines being formed in all cases.[11]

738. **Mixed Amines.** In this reaction the ammonia may be replaced by a *primary* aliphatic *amine* which gives us a method of preparing mixed secondary amines. It is sufficient to pass a mixture of a primary amine and an aliphatic, aromatic, or cyclohexyl alcohol in equivalent amounts over thoria at about 320°. Among the aliphatic alcohols, *methyl* gives the poorest results. *Ethyl-isoamyl-amine*, boiling at 126°, *propyl-isoamyl-amine*, boiling at 145°, and *isobutyl-isoamyl-amine*, boiling at 158°, have been prepared in this manner.[12]

[8] SABATIER and MAILHE, *Compt. rend.*, **153**, 160 (1911).
[9] SABATIER and MAILHE, *Compt. rend.*, **153**, 1204 (1911).
[10] MAILHE, *Bull. Soc. Chim.* (4), **15**, 327 (1914).
[11] SABATIER and MAILHE, *Compt. rend.*, **153**, 1204 (1911).
[12] SABATIER and MAILHE, *Compt. rend.*, **148**, 900 (1909).

739. By associating *cyclohexyl-amine* with various aliphatic alcohols, with benzyl alcohols, and with cyclohexanol and its homologs, a large number of mixed secondary cyclohexyl-amines can be prepared.[13]

Thus methyl alcohol gives *methyl-cyclohexyl-amine*, boiling at 145°, while *ethyl* and other primary alcohols give the corresponding mixed amines with still better yields. *Isopropyl-cyclohexyl-amine* [14] and *benzyl-cyclohexyl-amines* have been made thus.

Cyclohexanol itself gives *di-cyclohexyl-amine* identical with that obtained in the hydrogenation of aniline (466). The three *methylcyclohexanols* give the three methylcyclohexyl-cyclohexyl-amines.[15]

740. At higher temperatures the *aromatic amines* can undergo similar reactions. By passing over alumina at 400–430° a mixture of *aniline* vapors and *methyl alcohol* in excess, the immediate formation of *methyl-aniline* is obtained and of *dimethyl-aniline*, resulting from the action of the methyl alcohol on the methyl-aniline.

Likewise *o.toluidine* is completely transformed by methyl alcohol over thoria into *methyl-o.toluidine* and then into *dimethyl-o.toluidine*. Similar results are obtained with *meta* and *para toluidines*. A single passage over the catalyst produces about equal proportions of the mono- and di-methyl compounds, and a second passage completes the substitution.[16]

By causing ammonia to act on a mixture of two alcohols, the primary and secondary amines corresponding to each alcohol are obtained and some of the mixed secondary amine. This has been found true with a mixture of *propyl* and *isoamyl alcohols* at 330°.

741. **Alkyl-piperidines.** The above method can be applied to *piperidine* with various alcohols over thoria at 350°. The results are satisfactory with *propyl alcohol* which yields only a little propylene and gives *N-propyl-piperidine*, boiling at 149°, and with *isoamyl alcohol* which furnishes *N-isoamyl-piperidine*, boiling at 186°, but are poor with cyclohexanol which gives much cyclohexene and only a little *N-cyclohexyl-piperidine*, boiling at 216°.[17]

742. **Pyrrol.** An analogous reaction is carried out by the aid of zinc dust with a mixture of *ethyl alcohol* and *pyrrol* which give *α-ethyl-pyrrol*.[18]

[13] SABATIER and MAILHE, *Compt. rend.*, **153**, 1207 (1911).

[14] MAILHE and AMOROUX, *Bull. Soc. Chim.* (4), **15**, 777 (1914).

[15] SABATIER and MAILHE, *Compt. rend.*, **153**, 1207 (1911).

[16] MAILHE and DE GODON, *Compt. rend.*, **166**, 467 and 564 (1918).

[17] GAUDION, *Bull. Soc. Chim.* (4), **9**, 417 (1911).

[18] DENNSTEDT, *Berichte*, **23**, 2563 (1890). — ZANETTI, *Gaz. Chim. Ital.*, **21** (2), 167 (1891).

§ 4. — ELIMINATION OF WATER BETWEEN AN ALCOHOL AND HYDROGEN SULPHIDE

Synthesis of Mercaptans

743. If the direct action of alcohols on the dehydrating oxides, such as thoria, gives rise to the formation of a sort of unstable ester (*thorinate*), it can be predicted that when this is brought into contact with an acid more energetic than the hydrate of the oxide, such acid will displace the oxide at least in part to give a new ester. We will have:

$$\underset{\text{thorinate}}{ThO(OC_nH_{2n+1})_2} + 2AH = \underset{\text{ester}}{2A.C_nH_{2n+1}} + ThO_2 + H_2O$$
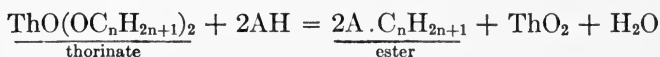
and if the acid is incapable of forming a stable salt with thoria as a base, the thoria will be regenerated and will react with a new portion of alcohol to repeat the cycle.

Sabatier and Mailhe believed that *hydrogen sulphide*, which does not react with thoria (nor with alumina), would act in this manner, since it appears to be a stronger acid than thoria. We would have in succession:

$$\underset{\text{thorinate}}{ThO(OC_nH_{2n+1})_2} + 2H_2S = \underset{\text{mercaptan}}{2C_nH_{2n+1}.SH} + ThO_2 + H_2O$$
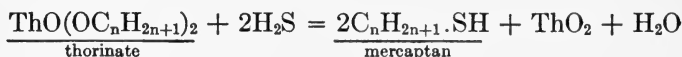
and then, with greater difficulty, on account of the acid function still remaining in the mercaptan:

$$\underset{\text{thorinate}}{ThO(OC_nH_{2n+1})_2} + 2C_nH_{2n+1}.SH = 2(C_nH_{2n+1})_2S + ThO_2 + H_2O.$$
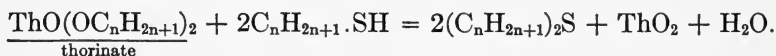
The thoria being regenerated can react with a fresh portion of alcohol and if the hydrogen sulphide continues to act, the thoria can function indefinitely as a catalyst to produce mercaptans and alkyl sulphides, provided that the reaction of the hydrogen sulphide on the unstable thorinate is more rapid than the decomposition of the thorinate into the *unsaturated hydrocarbon*, water and thoria.

744. Experiment has shown that this is usually the case. This is a *direct method for the preparation of mercaptans* from the alcohols. It is sufficient to pass a mixture of the alcohol vapors and hydrogen sulphide over a train of thoria maintained between 300 and 380°. The *mercaptan* along with a small amount of the neutral *sulphide* is condensed with the water and unchanged alcohol.

A portion of the alcohol is dehydrated to the unsaturated hydro-

carbon, but with the primary aliphatic alcohols this is not important, provided the reaction temperature is not too high, but it is considerable with the secondary alcohols which decompose into hydrocarbons more readily.

Methyl, ethyl, propyl, isobutyl, and *isoamyl mercaptans* have been thus prepared with yields above 75 %, so long as the condensation of the products is efficient. The yield is equally good for *allyl mercaptan* from allyl alcohol. Benzyl alcohol gives a rather large proportion of benzyl mercaptan and some sulphide.[19] [20]

745. The yields are less satisfactory, hardly above one third, when *secondary alcohols* are used. The following mercaptans have been obtained in this way: *propane-thiol (2), pentane-thiol (3), heptane-thiol (5), 2.4-dimethyl-pentane-thiol (3), cyclohexyl mercaptan* and the three *o.m. and p.methyl-cyclohexyl mercaptans,*[21] and also the *mercaptan* from *benzhydrol,* $C_6H_5.CH(SH).C_6H_5$, boiling at 278°.[22]

746. Various other catalytic oxides have been found to be inferior to thoria. With isoamyl alcohol and thoria maintained at 370–80°, the approximate yields of mercaptans for 100 parts of alcohol destroyed were:

Thoria	70
Zirconia	44
Uranous oxide	30
Blue oxide of tungsten	22
Chromic oxide	18
Blue oxide of molybdenum	17
Alumina	10

Alumina gives amylene chiefly.[23]

[19] SABATIER and MAILHE, *Compt. rend.,* **150,** 1217 (1910).

[20] Working at 360–380° KRAMER and REID [*J. Amer. Chem. Soc.* **43,** 887 (1921)], obtain the following yields from the alcohols named: methyl 42 %, ethyl 35 %, propyl 45 %, n.butyl 52 %, isobutyl 36 %, isoamyl 42 %. A part, at least, of the discrepancy between these figures and those given by Sabatier and Mailhe is due to a different method of estimating the mercaptan produced.

They find that the amounts of unsaturated hydrocarbons formed are surprisingly low, usually only 2 to 3 %, while considerable amounts of the aldehydes, 7 to 15 % (estimated by the hydrogen produced), are formed. — E. E. R.

[21] MAILHE, *Bull. Soc. Chim.* (4), **15,** 327 (1914).

[22] SABATIER and MAILHE, *Bull. Soc. Chim.* (4), **11,** 99 (1912).

[23] SABATIER and MAILHE, *Compt. rend.,* **150,** 1569 (1914).

§ 5. — ELIMINATION OF WATER BETWEEN ALCOHOLS AND ACIDS

Esterification

747. It is known that the formation of esters by the direct action of organic acids on alcohols takes place very slowly at ordinary temperatures and that the transformation is never complete as it is limited by the inverse action of water on the ester. Several years of contact are required for this limit to be reached. Elevation of the temperature hastens the reaction greatly but it still requires considerable time, several days at 110°, several hours at 156°.

The production of ester is very slow in the gaseous state also, even at temperatures above 250°: when a mixture of equivalent amounts of the vapors of ethyl alcohol and acetic acid is passed through a tube heated above 250°, the esterification effected is entirely negligible.

But either in the liquid or in the vapor condition, the presence of small amounts of *catalysts* accelerates the production of ester enormously so that the limit is soon reached.

Esterification by Catalysis in the Liquid State

748. The catalysts for esterification in liquid system are chiefly the strong *mineral acids*, hydrochloric and sulphuric, and several salts, *ammonium salts, alkaline bisulphates, zinc chloride, sodium acetate* mixed with water.

749. **Catalysis by Mineral Acids.** When equal molecules of ethyl alcohol and acetic acid are mixed and the mixture is distilled, the amount of ester produced is less than 1%.

But a long time ago, Berthelot found that it is sufficient to add to a mixture of an organic acid and an alcohol a few per cent of hydrochloric or sulphuric acid to cause an abundant formation of ethyl acetate, benzoate, etc.[24] He showed that traces of *sulphuric acid* are sufficient for the preparation of ethyl acetate.[25]

750. To a mixture of equal molecules of ethyl alcohol and acetic acid (106 g.) small quantities of hydrochloric acid were added, namely:

	To the first	0.67 g. or 0.017 molecule
	second	4.77 g. or 0.125 molecule
	third	11.84 g. or 0.33 molecule

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[24] BERTHELOT, *Bull. Soc. Chim.* (2), **31**, 342 (1879).
[25] BERTHELOT and JUNGFLEISCH, *Traité de Chim. Organ.*, 3rd Ed. 1886, I, 208.

The amounts of ester formed were as follows:

	At ordinary temperature		
	First	Second	Third
Immediately after mixing	9.6 %	58.7 %	82.3 %
After six hours	9.6	73.6	75.8

The limit without the mineral acid would be 66.6 %: this limit is raised by the presence of the hydrochloric acid,[26] and is practically attained in six hours with the above mixtures. In the cold, without this acid, several years would have been required. Besides, no ethyl chloride was formed.

751. Analogous results were obtained with sulphuric acid. To a mixture of 1 mol. ethyl alcohol, 1 mol. acetic acid and 0.5 mol. water was added 0.02 mol. (about 2 g.) sulphuric acid and in 24 hours in the cold, the esterification had reached 59.6 %. In 2 hours at 100°, 60.6 % was reached, which is the limit for this system.[27]

By boiling under reflux a mixture of 25 cc. *propionic acid*, 25 cc. *propyl alcohol*, and 50 cc. 5 % *sulphuric acid*, the proportion of ester was:[28]

After 0.5 hour	45.1 %
1 hour	51.8
2 hours	56.9
3 hours	58.3

752. The action of the sulphuric acid can be explained by the formation of *acid ethyl sulphate*, the immediate product of the action of the sulphuric acid, and the action of which on the acetic acid would produce ethyl acetate and regenerate sulphuric acid, which would renew the action. In the case of hydrochloric acid, Berthelot explains the accelerating action by assuming the formation of an addition product of the hydrochloric acid and the alcohol.[29] [30]

Bodroux has proposed a different explanation based on the temporary formation of an addition compound of the mineral acid cata-

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[26] BERTHELOT explained the elevation of the limit by the taking part of the hydrochloric acid in the equilibrium, in which it increases the total amount of acid relative to the alcohol.

[27] BERTHELOT, *Bull. Soc. Chim.* (2), **31**, 342 (1879).

[28] BODROUX, *Compt. rend.*, **157**, 939 (1913).

[29] BERTHELOT, *Bull. Soc. Chim.* (2), **31**, 342 (1879).

[30] It is curious how many chemists have given entirely different explanations for the action of hydrochloric and sulphuric acids. All the facts go to show that all acids act alike and that whatever explanation is given in any one case must fit all others. — E. E. R.

lyst with the organic acid considered as the anhydride of an ortho acid:

$$AH + R . C {\overset{\displaystyle /\!\!\!O}{\underset{\displaystyle \backslash OH}{}}} = R . C {\overset{\displaystyle /OH}{\underset{\displaystyle \backslash A}{-OH}}}$$

then:

$$R . C {\overset{\displaystyle /OH}{\underset{\displaystyle \backslash A}{-OH}}} + R'OH = AH + R . C {\overset{\displaystyle /OH}{\underset{\displaystyle \backslash OR'}{-OH}}}$$
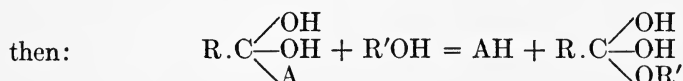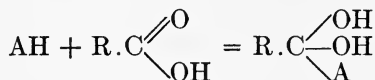
and finally by the immediate spontaneous loss of water: [31]

$$R . C {\overset{\displaystyle /\!\!\!(OH)_2}{\underset{\displaystyle \backslash OR'}{}}} = H_2O + R . CO . OR'.$$
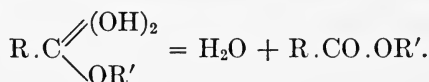
753. Many chemists still continue to think that the presence of a large amount of the mineral acid is favorable to esterification and it has become common usage to saturate the mixture of alcohol and acid with hydrogen chloride when preparing esters. Many seem to have forgotten that the same end can be attained by employing very small proportions of acids as catalysts. In 1895 Emil Fischer and Speier made exact measurements on this matter and showed that the use of small quantities of the mineral acids makes the operation more convenient and leads to satisfactory yields.[32]

754. Thus for the preparation of *ethyl benzoate*, the classical method was to saturate with hydrogen chloride a mixture of 1 part of benzoic acid with 4 parts ethyl alcohol, which gave only 73 % yield. Erdmann recommended heating on the water bath for 10 to 12 hours 1 part of the acid, 0.8 of alcohol and 0.4 of concentrated sulphuric acid, the yield being 75 %.

By dissolving 3 % hydrogen chloride in a mixture of 2 parts of alcohol to 1 part of acid, Emil Fischer obtained 76 % of the ester, while for 1 % hydrogen chloride, the yield was 64.5 % for the same time of heating.

755. The use of sulphuric acid is very advantageous. A mixture of 1 part of benzoic acid, 2 parts of alcohol and 0.2 part concentrated sulphuric acid is heated 3 hours under reflux and a practical yield of 90 % is obtained. If account is taken of inevitable losses during the washings, the yield is practically quantitative and as the excess of alcohol can be recovered almost entirely, the operation is very advantageous economically.

[31] BODROUX, *Compt. rend.*, **157**, 1428 (1913).
[32] E. FISCHER and SPEIER, *Berichte*, **28**, 3252 (1895).

756. Emil Fischer has shown that this process can be applied not only to the aliphatic acids as Berthelot had found, and to benzoic acid, but also to a large number of types of acids whether aliphatic or aromatic:

Monobasic acids (*naphthoic, phenyl-acetic*);
Unsaturated monobasic acids (*crotonic, cinnamic*);
Saturated dibasic acids (*succinic, phthalic*), or unsaturated (*fumaric*);
Hydroxy-acids (*glycolic, phenyl-glycolic*);
Phenol-acids (*salicylic*);
Ketone-acids (*laevulinic*);
Polybasic hydroxy-acids (*malic, tartaric, citric, mucic*).

The yields obtained are usually very satisfactory; we quote some of the results obtained by heating for 4 hours a mixture of 1 part of the acid with 3 to 4 parts of ethyl alcohol.

	% Catalyst	% Ester
α-Naphthoic acid	2.2 HCl	74.8
Phenyl-acetic	2.2 H_2SO_4	87.0
Cinnamic	0.7 HCl	78.8
Cinnamic	7.5 H_2SO_4	89.7
Crotonic	7.5 H_2SO_4	54.3
Phenyl-glycolic	2.2 HCl	67.5
Laevulinic.	0.7 HCl	76.5
Succinic.	0.8 HCl	73.9
Succinic.	8.0 H_2SO_4	73.9
Fumaric	0.8 HCl	68.2
Tartaric	0.8 HCl	72.8
Malic	0.8 HCl	70.5

757. To obtain slightly soluble esters, Bodroux adds to a mixture of an organic acid and alcohol its weight of pure commercial *hydrochloric acid* diluted with its own volume of water: in the cold the mixture becomes turbid in a few hours and finally gives 60 to 90 % of ester. This process works well for *phenyl-acetic acid* with various saturated alcohols but not so well for *benzoic, salicylic* and *cinnamic acids*.[33]

The yields are less satisfactory, hardly more than 50 %, with *allyl alcohol* or with the secondary alcohols, *isopropyl* and *cyclohexyl*. They are worse still with *dimethyl-ethyl-carbinol* as well as with *glycerine* and *mannite*.[34]

[33] BODROUX, *Compt. rend.*, **157**, 939 (1913).
[34] BODROUX, *Compt. rend.*, **157**, 1428 (1913).

758. Senderens and Aboulenc, who do not seem to have known of the work of Berthelot and of Emil Fischer, have described as new the method of direct esterification of alcohols in presence of small amounts of sulphuric acid. The results which they give are a verification and extension to other alcohols of a part of the results of Emil Fischer. But they have thought that they were able to make an essential distinction in the mechanism of the reaction between the aromatic acids that can be regarded as substitution products of acetic acid, e.g. *phenyl-acetic*, on the one side and straight aromatic acids in which the carboxyl is attached to the nucleus, e.g. *benzoic and toluic*, on the other.

For the first class, they consider the speed of the esterification and the amount of ester formed as independent of the amount of the sulphuric acid, while for benzoic acid, for example, these increase with the amount of the acid, *"which consequently does not act simply as a catalyst."*

This distinction can not be admitted. A solid catalyst, up to a certain limit, acts in proportion to its active surface. Soluble catalysts, such as diastases or acids in hydration reactions, or sulphuric acid in this case, act proportionally to their mass, at least if this is not too large for the total volume of liquid, and this is as true for acetic as for benzoic. The results quoted above from Berthelot for the formation of ethyl acetate in the presence of hydrochloric acid, show that, in the cold, the rapidity of the esterification is approximately proportional to the amount of the catalyst.

The difference between the aliphatic acids and their analogs and benzoic acid is that the velocity of the esterification of the former by the catalytic acid is much greater than for benzoic.[35] To obtain the same yield of ester from benzoic a larger amount of the catalyst would have been required.

Oxalic acid is esterified regularly like succinic.

Furthermore the practical yields are much better with the higher alcohols since with the less soluble esters the losses in the necessary washings with water and alkaline carbonate solutions are less serious.

759. According to the same authors the *sulphuric acid* can be replaced by double its weight of *anhydrous aluminum sulphate* or *potassium bisulphate*.[36]

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[35] The slowness of esterification of benzoic acid as compared with acetic acid is shown by the work of FREAS and REID, [(*J. Amer. Chem. Soc.*, **40**, 569 (1918)], who found it necessary to heat benzoic acid with methyl and ethyl alcohols to 200° for 96 hours to insure reaching the limit of esterification while BERTHELOT and ST. GILLES found 24 hours sufficient even at 170°. — E. E. R.

[36] SENDERENS and ABOULENC, *Compt. rend.*, **152**, 1671 and 1855 (1911) and **153**, 881 (1911).

760. *Glycerine* mixed with *acetic acid* (1 molecule of glycerine to 3 of the acid) gives on boiling under reflux for 1 hour, esterification amounting to 0.4 molecule of acid: by the addition of 5 % *potassium bisulphate*, the amount esterified reaches 1.2 molecules.

With 2 % *anhydrous aluminum sulphate* . . . . . . 1.5 mol.
      1 % *sulphuric acid* . . . . 1.5 mol.

By starting with 1 molecule of glycerine and 12 acetic acid, the amount esterified by boiling 1 hour is:

With the aluminum sulphate . . . . 2 mol. acid
    sulphuric acid . . . . 3 mol. acid

Triacetine is thus reached and there would be no advantage in increasing the amount of the catalyst.[37]

761. **Esterification by Acetanhydride.** A common method of preparing the acetates of alcohols or of poly-alcohols is to heat them with acetanhydride.

$$R.OH + (CH_3.CO)_2O = 2CH_3.CO_2R + H_2O.^{38}$$
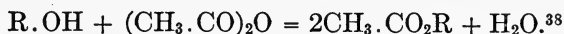
By this means all the hydroxyl groups of a complex molecule are esterified. The presence of a certain amount of sodium acetate favors the action of the anhydride.

Still better results are obtained by adding to an alcohol four times its weight of acetanhydride and a small fragment of *fused zinc chloride*. The reaction becomes very rapid immediately. In the case of *glycerine* a veritable explosion is caused. With *mannite*, however, it is regular and yields in a few minutes *mannite hexa-acetate*, melting at 120°.[39]

Catalytic Esterification in Gaseous System

762. The assumption of an unstable combination between the dehydrating oxides and the alcohols has been a basis for the prediction of various reactions which have been realized by experiment, such as the formation of mercaptans and aliphatic amines. Sabatier and Mailhe thought that it might be expected that these combinations

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[37] SENDERENS and ABOULENC, *Compt. rend.*, **158**, 581 (1914).
[38] I think it better to write the reaction thus:

$$R.OH + (CH_3.CO)_2O = CH_3CO_2R + CH_3CO_2H.$$
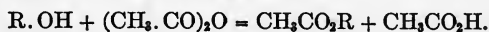
An excess of the anhydride is always used and the reaction goes to completion since no water is formed to reverse it. — E. E. R.
[39] FRANCHIMONT, *Berichte*, **12**, 2059 (1879).

would play a part analogous to that of the acid sulphuric esters, that is, that the dehydrating oxides would act as *esterification catalysts*.[40]

763. As has already been indicated, if a mixture of the vapors of an alcohol and an organic acid be passed through a 60 cm. tube heated between 300 and 360°, the proportion of ester formed during the passage is absolutely negligible, but the presence of a *catalytic oxide* changes the case entirely. Let us suppose that the tube contains a catalytic oxide, MO, derived from the metallic hydroxide, $M(OH)_2$, an amphoteric hydroxide.

The reaction can take three different courses:

1st. The acid may combine to form a salt, unstable for those oxides which catalyze acids, and breaking down to regenerate the oxide and forming a symmetrical ketone (837):

(1) $MO + 2R.COOH = H_2O + (R.COO)_2M = H_2O + MO + CO_2 + \underset{\text{ketone}}{\underline{R.CO.R}}.$
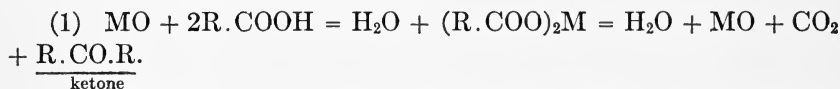
2nd. The oxide may combine with the alcohol to form an unstable salt :

$$MO + 2C_nH_{2n+1}.OH = H_2O + M(OC_nH_{2n+1})_2.$$
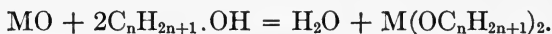
This unstable complex can decompose in two ways, either by itself to give the unsaturated hydrocarbon: [41]

(2) $M(OC_nH_{2n+1})_2 = MO + H_2O + 2C_nH_{2n}$
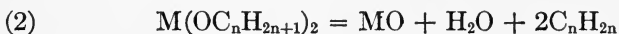
or with the aid of the acid to form an ester:

(3) $M(OC_nH_{2n+1})_2 + 2R.CO.OH = MO + H_2O + 2R.CO.OC_nH_{2n+1}.$
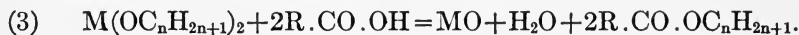
In any case the catalytic oxide is regenerated and can continue the same effects. Furthermore in reaction (3), the water produced tends to destroy the combination, $M(OC_nH_{2n+1})_2$, and consequently *limits* the formation of the ester which results from it. Since these reactions are very rapid, the esterification limit will be reached quickly, the catalytic oxide acting like the platinum sponge in the combination of iodine and hydrogen (19).

764. We may have simultaneously formation of a *ketone*, production of unsaturated hydrocarbon (or ether), and the rapid reversible formation of the ester; this is what is observed when a mixture of the vapors of ethyl alcohol and acetic acid is passed over *thoria* or *alumina* heated to about 400°.

If the conditions are such that reactions (1) and (2) do not take place, (3) will be the only one and we will have an advantageous catalytic formation of ester.

[40] SABATIER and MAILHE, *Compt. rend.*, **150**, 823 (1910).
[41] In the case of methyl alcohol, this decomposition gives methyl ether.

To obtain this result it is necessary to operate at such low temperatures that the acids are not decomposed and that the decomposition into unsaturated hydrocarbon is not too rapid.

765. Thoria, which is the most active catalyst for the destruction of *acids* and which, likewise, has a powerful dehydrating effect on alcohols, would doubtless be less advantageous than *titania*, which produces these effects less vigorously.

766. With *aromatic* acids, such as benzoic and its homologs which have the carboxyl attached to the nucleus, thoria does not produce any appreciable decomposition even up to 450° : it can be predicted that reaction (1) will not take place. Experiment has shown that this is the case and that at 350° reaction (2) is negligible as compared with reaction (3), which goes very rapidly. By vaporizing a saturated solution of *benzoic acid* in an alcohol (there are at least 12 molecules of the alcohol to 1 of the acid) and passing the vapors over a train of thoria at 350°, there is no appreciable formation of the unsaturated hydrocarbon, but the benzoic acid is almost totally esterified. *Methyl, ethyl, propyl, butyl, isobutyl, isoamyl* and *allyl benzoates* have been obtained advantageously in this way.

In spite of their greater tendency to form unsaturated hydrocarbons, the secondary alcohols can form benzoic esters with fairly good yields : this is the case with *isopropyl alcohol* with which the formation of propylene is of minor importance. Cyclohexyl alcohol is more delicate, but nevertheless gives a fairly good yield of the benzoate.

Analogous results are obtained with the three *toluic acids* which are readily esterified by thoria at 350–380°, but the practical preparation of these esters is less advantageous on account of the smaller solubility of these acids, particularly the *para*, in the alcohols: the meta is the most soluble.[42]

767. Titania enables us to esterify various acids in the same manner. If a mixture of equivalent amounts of the vapors of a primary alcohol and an aliphatic acid, other than formic, is passed over a train of this oxide maintained at 280–300°, rapid esterification takes place, reaching a limit slightly above that observed by Berthelot and Menschutkin in their experiments on direct esterification. The production of gas on account of the destruction of the acid or the alcohol is absolutely negligible.

768. It is known that the presence of a catalyst does not change the location of the limit in reversible reactions, but diminishes greatly the time required to reach that limit. In this particular case, Berthe-

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[42] Sabatier and Mailhe, *Compt. rend.*, **152**, 358 (1911).

lot found that the limit is moved somewhat by elevation of the temperature. For equivalent amounts of ethyl alcohol and acetic acid, he found the following values of the limit:

In the cold (10 years)	65.2 %
At 100° (200 hours)	65.6
170° (42 hours)	66.5
200° (24 hours)	67.3

The figures show that the limit is not fixed but progresses slowly with the temperature and suggest a still higher value for the limit at 280–300°.

769. At 155°, Menschutkin found for various alcohols mixed with equivalent amounts of different acids, the following limits: [43]

Acetic acid	+ methyl alcohol	69.6 %
Acetic acid	+ ethyl alcohol	66.6
Acetic acid	+ propyl alcohol	66.9
Acetic acid	+ butyl alcohol	67.3
Acetic acid	+ isobutyl alcohol	67.4
Propionic acid	+ isobutyl alcohol	68.7
Butyric acid	+ isobutyl alcohol	69.5
Isobutyric acid	+ isobutyl alcohol	69.5

Sabatier and Mailhe obtained the following limits with titania at 280–300°:

Acetic acid	+ isobutyl alcohol	69.5 %
Propionic acid	+ methyl alcohol	72.9
Propionic acid	+ isoamyl alcohol	72
Butyric acid	+ ethyl alcohol	71
Butyric acid	+ isoamyl alcohol	72.7
Isobutyric acid	+ ethyl alcohol	71

These values are slightly higher than the corresponding figures obtained at lower temperatures.

770. Furthermore, in this rapid catalytic esterification, the same laws are found to hold as Berthelot formulated for direct esterification. An *excess* of *one constituent* increases the amount of the other combined. Thus for 1 molecule of isobutyric acid with 1, 2, and 4 molecules of ethyl alcohol, the following percentages of the acid were esterified:

With 1 molecule	71.0 %
2 molecules	83.5
4 molecules	91.0

[43] MENSCHUTKIN, *Ann. Chim. Phys.* (5), **20**, 289, and **23**, 64 (1880).

In the presence of more than 10 molecules of alcohol the esterification of the acid is nearly complete and, conversely, almost all of the alcohol is esterified by a large excess of the acid. The relative cost of the alcohol and acid in such cases decides which conditions are most economical.

771. Sabatier and Mailhe have prepared easily the *methyl, ethyl, propyl, butyl, isobutyl* and *isoamyl* esters of *acetic, propionic, butyric, isobutyric, isovaleric, caproic, pelargonic* and *crotonic*, etc., acids.

Benzyl alcohol gives equally good results with various acids. The dehydration to the resinous hydrocarbon, $(C_7H_6)_x$, which is effected so rapidly by catalytic oxides, hardly takes place at all in the presence of acid vapors.[44]

772. Sabatier and Mailhe have found further that it is not indispensable to use as high a temperature as 280°, which is usually the most advantageous.

The catalytic activity continues, though it falls off gradually, to temperatures much lower where the acids and alcohols are stable. In this *titania* is superior to thoria.[45] By operating with equal molecules of ethyl alcohol and acetic acid and passing the vapors over a 50 cm. train of the oxide at the rate of 0.2 molecule, or 21 g., per hour, Sabatier and Mailhe obtained the following percentages of esterification:

	With thoria	With titania
At 150°.	11 %	. . . 20 %
170°.	26	. . . —
230°.	45	. . . 60

Besides, the catalytic power of titania persists almost indefinitely; it was not diminished by experiments on varied mixtures of alcohols and acids extending over 20 days.

773. **Formic acid** can be esterified at these temperatures at which it is fairly stable. By operating with equal molecules of formic acid and ethyl alcohol, distributed by the same capillary tube through which the molecular volume passed very rapidly, in spite of this unfavorable circumstance, the following amounts were esterified over titania:

At 120°	47 %
150°	65 %

The esterification limit is nearly reached even at 150° at which the decomposition of formic acid into gaseous products is still inconsiderable.

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[44] SABATIER and MAILHE, *Compt. rend.*, **152**, 494 (1911).

[45] MAILHE and DE GODON [(*Bull. Soc. Chim.*, **29**, 101 (1921)] conclude that ZrO_2 is as good as or better than TiO_2. MILLIGAN and REID (unpublished work) find silica gel to be a better esterification catalyst than either. — E. E. R.

In practice formic acid, mixed with an excess of the desired alcohol, is passed over thoria at 150°. *Methyl, ethyl, propyl, butyl, isoamyl* and *benzyl for mates* have been readily prepared in this way.

774. The comparison of these results has led Sabatier and Mailhe to conclude that the rapidity of the esterification of the primary alcohols by the aliphatic acids, in presence of catalysts, is directly proportional to the *kinetic velocities* of the reacting molecules; *it is as much greater as the molecules are lighter* and it can be inferred that the reason is to be found in the greater rapidity of gaseous interchanges on the catalyst.

775. The secondary alcohol, *isopropyl*, mixed with *isobutyric acid* does not give any evolution of propylene with titania below 300°. The proportion esterified was:

At 235° . . . . 16.5 %
256° 21
292° 37

For primary *propyl* alcohol, the amount is 50 % at 235° and 72 % at 292°.

776. **Trimethyl-carbinol** (tertiary butyl alcohol) likewise mixed with isobutyric acid, gives 6 % ester at 235° with no formation of the hydrocarbon. With the isomeric primary alcohol, *isobutyl*, it is 22 %. It is only at 255° that the decomposition into butylene begins to manifest itself. At 265° it is quite rapid and the acidity of the mixture increases on account of the destruction of the alcohol in place of diminishing by esterification.

777. These results agree well with the weakening of the alcoholic function in secondary and particularly in tertiary alcohols. The velocity of the catalytic esterification should be at the same time a function of the speed of the gaseous interchanges, in consequence of the smallness of the molecules and also of the facility with which the alcohol forms the temporary unstable complexes with the catalytic oxide.[46]

778. **Beryllium oxide** also can be employed as an esterification catalyst. With this oxide heated to 310°, yields of above 70 % of ester can be obtained. The catalyst can be regenerated by calcining at a red heat. With this catalyst esters of tertiary alcohols and of high molecular weight acids can be prepared.[47][48]

[46] SABATIER and MAILHE, *Compt. rend.*, **152**, 1044 (1911).
[47] HAUSER and KLOTZ, *Chem. Zeit.*, **37**, 146 (1913).
[48] I have tried to prepare esters by the use of beryllia and so has Dr. MILLIGAN but neither of us has been able to verify the statements of HAUSER and KLOTZ. — E. E. R.

§ 6. — ELIMINATION OF WATER BETWEEN ALCOHOLS AND ALDEHYDES OR KETONES

779. The elimination of water between alcohols and aldehydes or ketones can take place in several ways. The one way is to a certain extent comparable to *esterification* and leads to *acetals;* it can hardly be realized except in liquid systems. The other, more exceptional, gives rise to *hydrocarbons* and is effected in gaseous systems.

I. — Formation of Acetals

780. Aldehydes can combine directly with alcohols to give acetals:

$$\underbrace{R.CHO}_{\text{aldehyde}} + \underbrace{2R'OH}_{\text{alcohol}} = H_2O + \underbrace{R.CH(OR')_2}_{\text{acetal}}.$$
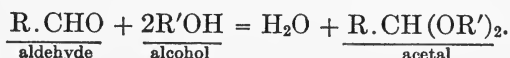
But the direct formation is very imperfect, unless suitable *catalysts* are used.

Good yields are obtained by passing for a long time a current of pure *phosphine* through a well cooled mixture of the aldehyde and alcohol: by this means *acetaldehyde* has been made to combine with *ethyl, propyl* and *isobutyl* alcohols.[49]

The combination of alcohols and aldehydes is greatly aided by the presence of a certain amount of glacial *acetic acid*.[50]

781. Trioxymethylene, the condensation product of formaldehyde, readily forms methylal, $HCH(OCH_3)_2$, when it is mixed with *methyl alcohol* and heated on the water bath for 10 hours with 3 % of ferric chloride.

782. A good method for preparing acetals is to mix the aldehyde with the proper amount of alcohol containing 1 % of *hydrogen chloride* (the gas dissolved) and digest the mixture for 18 to 20 hours: the yields are usually satisfactory.[51]

To obtain acetals from *acetaldehyde* with various aliphatic alcohols, 40 g. of acetaldehyde is mixed with 60 g. of the alcohol and 1 cc. concentrated *hydrochloric acid* is added and this mixture digested 24 hours with a saturated solution of sodium chloride and 10 g. of the solid salt.[52]

783. The action of *ethyl ortho-formate* on aldehydes or ketones readily produces their combinations with ethyl alcohol; but this re-

[49] ENGEL and GIRARD, *Jahresb.*, **1880**, 694.
[50] GEUTHER, *Annalen*, **126**, 62 (1863).
[51] E. FISCHER and GIEBE, *Berichte*, **30**, 3053 (1897).
[52] KING and MASON, *English patent*, 101,428 of 1916, *J. Soc. Chem. Ind.*, **35,** 1131 (1916).

action does not take place without the aid of suitable catalysts. These may be quite varied, e.g. *strong mineral acids, ferric chloride, ammonium chloride, ethyl-, diethyl-,* or *triethyl-amine hydrochlorides, potassium bisulphate, ammonium sulphate* or *nitrate.* Boiling for a few minutes is sufficient to assure the formation.

Thus to prepare the acetal from *ethyl alcohol* and *benzaldehyde,* 1 molecule of the aldehyde is mixed with 0.1 molecule ethyl ortho-formate and poured into 3 molecules of the alcohol and a little dry hydrogen chloride is passed in. After ten minutes boiling, the acetal, $C_6H_5 . CH (OC_2H_5)_2$ is obtained in 99 % yield. By using 2 g. ammonium chloride, the yield is 97 %.

The diethyl acetal of *acetone* is obtained thus with 66 % yield.

If the boiling is prolonged too greatly, the yield is more and more diminished, which shows that the catalyst tends to destroy by hydrolysis the acetal which it has formed.[53]

II. — Formation of Hydrocarbons in Gaseous System

784. The dehydrating action of oxides such as *alumina* on a mixture of an alcohol and an aldehyde can eliminate all of the oxygen as water producing a doubly unsaturated hydrocarbon.

This takes place when a mixture of *ethyl alcohol* and *acetaldehyde* is passed over the impure *alumina* formed by calcining ammonium alum. *Butadiene,* boiling at 2°, is obtained:

$$CH_2OH . CH_3 + OCH . CH_3 = 2H_2O + CH_2 : CH . CH : CH_2.$$
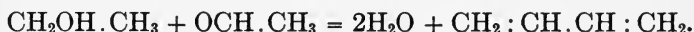
With pure alumina, *methyl-allene,* $CH_3 . CH : C : CH_2$, is also formed. This reaction can be applied to the synthesis of rubber by the polymerization of the hydrocarbon obtained (213). From 100 g. of the mixture of aldehyde and alcohol, 25 g. of the crude hydrocarbon may be obtained or 16 to 18 g. of pure butadiene which may be totally transformed into rubber.[54]

Similarly acetaldehyde, with *isopropyl* or *propyl alcohols,* leads to *piperylene,* $CH_3 . CH : CH . CH : CH_2$, boiling at 42°.[54]

[53] CLAISEN, *Berichte,* **40**, 3903 (1907).
[54] OSTROMUISSLENSKII and KELBASINSKI, *J. Russian Phys. Chem. Soc.,* **47**, 1509 (1915); *C. A.,* **10**, 3179 (1916).

CHAPTER XVII

DEHYDRATION (Continued)

§ 7. — DEHYDRATION OF PHENOLS ALONE

785. One method of preparing *ethers* from *phenols* is to distil dry aluminum phenylates: this works well for phenyl ether and for the ethers of ortho and para cresols.[1] This method of preparation leads us to foresee that phenyl ethers can be prepared catalytically by the action of a catalytic oxide such as thoria on the vapors of the phenol at a suitable temperature, the mechanism of dehydration depending, as with the alcohols, on the formation of an unstable thorinate which decomposes regenerating thoria.

We have: $2C_6H_5 . OH + ThO_2 = H_2O + \underset{\text{thorinate}}{\underline{Th(OC_6H_5)_2}}$

and then: $Th(OC_6H_5)_2 = ThO_2 + \underset{\text{ether}}{\underline{(C_6H_5)_2O}}.$

This prediction having been verified, Sabatier and Mailhe have based on it an *advantageous method* for the preparation of *phenol ethers* by the use of thoria.[2]

786. **Simple Phenol Ethers.** The vapors of the phenol are passed over a train of thoria kept at 400–500°. If the phenol is a liquid, it is introduced directly by means of the capillary tube (181); if it is a solid, its benzene solution is used. The reaction products are shaken with caustic soda, which extracts the unchanged phenol leaving the ether which is obtained entirely pure by one distillation. *Phenyl ether* can be prepared in this way very economically and in great purity with a yield of 50 % or better; meta and para cresyl ethers can be readily obtained, while ethers are more difficult to obtain from *ortho cresol* and from *xylenol (1,3,4)*,[3] and poor results are gotten with *carvacrol.*[4]

787. **Diphenylene Oxides.** This method leads to the simultaneous formation of *diphenylene oxides*, fluorescent compounds, less volatile than the ethers, and formed by the loss of H_2.

With ordinary phenol at 475°, there is formed along with phenyl

[1] GLADSTONE and TRIBE, *J. Chem. Soc.*, **41**, 9 (1882), and **49**, 25 (1886).

[2] SABATIER and MAILHE, *Compt. rend.*, **151**, 492 (1910).

[3] SABATIER and MAILHE, *Bull. Soc. Chim.* (4), **11**, 843 (1912).

[4] SABATIER and MAILHE, *Compt. rend.*, **158**, 608 (1914).

ether, boiling at 253° and melting at 28°, a considerable amount of

diphenylene oxide, $\begin{array}{c} C_6H_4 \\ | \\ C_6H_4 \end{array}\Big\rangle O$, boiling at 287° and melting at 85°, which

had previously been obtained by distilling calcium phenylate.[5] The *cresols, xylenols,* and *naphthols* give rise to the formation of similar products.[6]

788. **Mixed Phenol Ethers.** By dehydrating over thoria, not a single phenol, but a mixture of two phenols, the product contains along with the simple ethers of the two phenols and the diphenylene oxides, an amount, usually · considerable, of the mixed ether derived from the two phenols which can be separated by careful fractionation. Sabatier and Mailhe have prepared the following mixed ethers, *phenyl-o.cresyl, phenyl-m.cresyl, phenyl-p.cresyl, phenyl-α-naphthyl, phenyl-β-naphthyl, phenyl-carvacryl, p.cresyl-carvacryl,* as well as the phenylene-naphthylene oxides.[7]

§ 8. — ELIMINATION OF WATER BETWEEN PHENOLS AND ALCOHOLS

Synthesis of Alkyl Phenol Ethers

789. Sabatier and Mailhe have shown that catalytic oxides such as thoria readily eliminate water from a phenol and an alcohol with the formation of a mixed ether.[8] This is a *very advantageous method of preparing mixed ethers.* All that is necessary is to pass a mixture of the phenol with an excess of the alcohol over thoria at 390–420.° With *methyl alcohol,* which is dehydrated by thoria very slowly, the results are particularly good. The excess of the alcohol and most of the unchanged phenol are separated from the ether by fractionation. The remainder of the phenol is extracted by caustic soda from the mixed ether, which is purified by a single distillation.

In this way, Sabatier and Mailhe have prepared the methyl ethers of *phenol,* the three *cresols, xylenol(1,3,4), thymol, carvacrol,* and *α-* and *β-naphthols.*

At the same time small quantities, more or less important according to the phenol, of the *phenol ether* and *diphenylene oxide* are obtained. A mixture of *methyl alcohol* and *carvacrol* gives methyl-carvacryl ether, along with *di-carvacryl ether* and *carvacrylene.*[9]

[5] NIEDERHÄUSERN, *Berichte,* **15,** 1120 (1882).

[6] SABATIER and MAILHE, *Compt. rend.,* **151,** 494 (1910).

[7] SABATIER and MAILHE, *Compt. rend.,* **155,** 260 (1912), and **158,** 608 (1914).

[8] SABATIER and MAILHE, *Compt. rend.,* **151,** 359 (1910).

[9] SABATIER and MAILHE, *Compt. rend.,* **158,** 608 (1914).

The other alcohols, in spite of their own rapid decomposition by thoria, can readily give the mixed ethers : one operates around 420° on phenol dissolved in excess of the alcohol, a part of which is decomposed forming the unsaturated hydrocarbon. *Ethyl-, propyl-,* and *isoamyl-phenyl* ethers have been prepared in this way.

§ 9. — ELIMINATION OF WATER BETWEEN A PHENOL AND AN AMINE

790. Nothing worth while is accomplished by passing a phenol and ammonia over a catalytic oxide at 400°. The production of amines is quite negligible.

We may mention as a catalytic reaction of this sort, the action of *α-* and *β-naphthols*, on *aniline*, the *toluidines* and other aromatic amines, when they are heated 7 hours to about 200° in the presence of 1 % of *iodine*. The corresponding secondary amines are obtained with satisfactory yields.[10]

§ 10. — ELIMINATION OF WATER BETWEEN PHENOLS AND HYDROGEN SULPHIDE

791. Sabatier and Mailhe have found that by passing the vapors of a phenol and hydrogen sulphide over thoria between 430 and 480°, the corresponding *thiophenol* is obtained:

$$C_6R_5.OH + H_2S = H_2O + C_6R_5.SH.$$
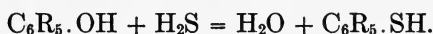
But the yield is not so good as with alcohols (744), and is not above 10 % in the most favorable case. A temperature of 500° decreases the yield on account of the serious decomposition of the hydrogen sulphide. Hence the reaction is of no practical use but is of only scientific interest.[11]

The yields are still less when other oxides are used. With *phenol*, the following yields were obtained at 450°:[12]

Alumina	0.4 %
Zirconia	1.5
Blue oxide of molybdenum	1.8
Blue oxide of tungsten	1.5
Chromic oxide.	2.5
Uranous oxide	3.8
Thoria	8.0

[10] KNOEVENAGEL, *J. prakt. Chem.* (2), **89,** 16 (1914).
[11] SABATIER and MAILHE, *Compt. rend.,* **150,** 1220 (1910).
[12] SABATIER and MAILHE, *Compt. rend.,* **150,** 1570 (1910).

§ 11. — ELIMINATION OF WATER BETWEEN PHENOLS AND ALDEHYDES

792. For some years there has been prepared under the name of *bakelite,* a resinous material very resistant to shock and to pressure and endowed with insulating properties of the first order. It results from the condensation of *phenol* or *cresols* with *formaldehyde* in the presence of various catalysts, chiefly substances with alkaline reaction.[13] According to Baekeland,[14] who has given his name to the product, one of the materials, called *bakelite* C, results from the reaction of 7 molecules of formaldehyde with 6 of phenol:

$$6C_6H_5OH + 7CH_2O = C_{43}H_{38}O_7 + 6H_2O.$$
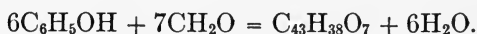
The formaldehyde can be replaced by *methylal, trioxymethylene,* or *hexamethylene-tetramine.*

The products obtained are very variable according to the operating conditions and either liquid intermediate substances or solids corresponding to an advanced stage of molecular condensation may be obtained. The condensation to the solid products can be effected by acid catalysts such as *hydrochloric* acid.

§ 12. — FORMATION OF PHENOLIC GLUCOSIDES

793. **Quinoline** employed in small proportion causes *phenols* to react with *acetyl-brom-glucose* forming the acetylate of the corresponding *phenyl-glucoside.* By warming for 1 hour 50 g. acetyl-bromglucose with 160 g. phenol in the presence of 19 g. quinoline, the *tetra-acetyl-phenyl-glucoside* is obtained, the hydrolysis of which by baryta water separates the phenyl-glucoside.[15]

§ 13. — DEHYDRATION OF ALDEHYDES OR OF KETONES

794. Frequently the presence of certain substances causes the condensation of two or more molecules of aldehydes or of ketones with the elimination of water and the formation of a single molecule retaining only one aldehyde or ketone group and containing double bonds.[16]

[13] LEBACH, *J. Soc. Chem. Ind.,* **32,** 559 (1913). — *Caoutchouc and Gutta-percha,* **14,** 9339 (1917). HUTIN, *Ibid.,* **16,** 9987 (1919).

[14] BAEKELAND, *J. Ind. Eng. Chem.,* **1,** 149 (1909).

[15] E. FISCHER and VON MECHEL, *Berichte,* **49,** 2813 (1916).

[16] SABATIER and MAILHE, *Compt. rend.,* **150,** 1220 (1910).

This process is called *crotonization* from *croton aldehyde* which is formed from *acetaldehyde*:[17]

$$CH_3.CHO + CH_3.CHO = H_2O + CH_3.CH:CH.CHO.$$
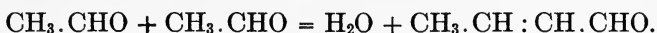
Reactions of this kind can take place between molecules of different aldehydes or ketones.

Crotonization in Liquid Medium

795. The catalysts that are able to cause the crotonization of aldehydes and ketones in liquid medium are quite varied and their action is generally quite slow : *soda, potash, hydrochloric acid, zinc chloride, lime, aluminum chloride* and *sodium acetate* may be mentioned.

In order to transform *acetaldehyde* into *croton aldehyde*, it is heated to 97° for 36 hours with 20 % of its weight of a water solution of *sodium acetate*,[18] or better to 100° for 48 hours with a solution of *zinc chloride*.[19]

Paraldehyde in contact with *sulphuric acid* also gives croton aldehyde.[20]

The same process applies to the crotonization of *propionic aldehyde* which can be crotonized by heating with a solution of *caustic soda*.[21] The same agent is employed for *butyric aldehyde*.[22] Dry hydrogen chloride [23] or a solution of sodium acetate may be used to crotonize *isobutyric aldehyde*.[24]

Zinc chloride, or alcoholic potash, causes two or four molecules of *heptaldehyde* to condense.[25] Contact with *zinc* turnings is sufficient to crotonize *isovaleric aldehyde: sodium*, caustic potash and hydrochloric acid produce the same effect.[26]

796. **Croton aldehyde** itself mixed with *acetaldehyde* and *zinc chloride* at 100°, undergoes a second like reaction and forms *hexadienal* (boiling at about 172°).[27]

$$CH_3.CH:CH.CHO + CH_3.CHO =$$
$$H_2O + CH_3.CH:CH.CH:CH.CHO.$$
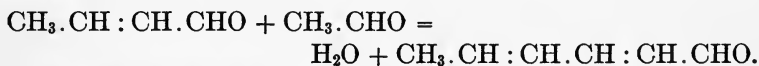
[17] SABATIER and MAILHE, *Compt. rend.*, **150**, 1570 (1910).

[18] LIEBEN, *Monatsh.*, **13**, 519 (1892).

[19] MÜLLER, *Bull. Soc. Chim.* (3), **6**, 796 (1891).

[20] DELÉPINE, *Ann. Chim. Phys.* (8), **16**, 136 (1909), and **20**, 389 (1910).

[21] HOPPE, *Monatsh.*, **9**, 637 (1888).

[22] RAUPENSTRAUCH, *Monatsh.*, **8**, 112 (1887).

[23] ŒCONOMIDÈS, *Bull. Soc. Chim.* (2), **36**, 209 (1881).

[24] FOSSEK, *Monatsh.*, **2**, 616 (1881).

[25] PERKIN, *Berichte*, **15**, 2804 (1882).

[26] RIBAN, *Bull. Soc. Chim.* (2), **18**, 64 (1872). — KEKULÉ, *Berichte*, **3**, 135 (1870). — BORODIN, *Berichte*, **6**, 983 (1873).

[27] KEKULÉ, *Annalen*, **162**, 105 (1872).

797. Ordinary *acetone*[28] kept for a long time in contact with lime,[29] or *aluminum chloride*[30] is transformed into *mesityl oxide:*

$$(CH_3)_2 : CH . CO . CH_3$$

and then into *phorone:*

$$(CH_3)_2C : CH . CO . CH : C(CH_3)_2.$$

Cyclohexanone, in contact with sodium ethylate or hydrochloric acid, condenses to an oily compound similar to mesityl oxide,[31]

$$CH_2 \Big\langle {CH_2 . CO \atop CH_2 . CH_2} \Big\rangle C : C \Big\langle {CH_2 . CH_2 \atop CH_2 . CH_2} \Big\rangle CH_2.$$
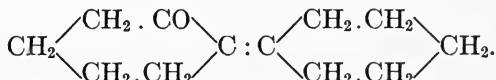
798. Crotonization can take place in a similar manner between different molecules, principally between a molecule of acetone and one or two molecules of aldehyde. The presence of aqueous or alcoholic soda is most frequently efficient in causing these condensations with the elimination of one or two molecules of water giving compounds containing a ketone group and one or two double bonds.

Benzaldehyde gives such products readily. Thus with acetone in prolonged contact with aqueous soda, it forms successively benzal-acetone and dibenzal-acetone:[32]

$$C_6H_5 . CHO + H_2CH . CO . CH_3 = H_2O + C_6H_5 . CH : CH . CO . CH_3$$

and

$$2C_6H_5 . CHO + CH_3 . CO . CH_3 = 2H_2O + (C_6H_5 . CH : CH)_2CO.$$
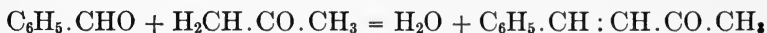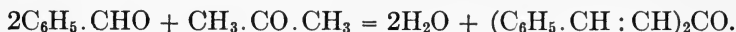
In the presence of a little soda solution, *o.nitrobenzaldehyde* condenses with acetone to give *o.nitrobenzal-acetone:*[33]

$$O_2N . C_6H_4 . CHO + CH_3 . CO . CH_3 =$$
$$H_2O + O_2N . C_6H_4 . CH : CH . CO . CH_3.$$
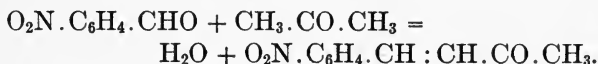
799. Benzaldehyde condenses with *acetophenone* in the presence of hydrogen chloride,[34] or of a few cubic centimeters of sodium methylate,[35] to give *diphenyl-propenone,* $C_6H_5 . CH : CH . CO . C_6H_5.$

[28] Pure acetone passed over heated freshly prepared alumina forms condensation products, only about 60 % of the acetone passing through unchanged. No gaseous products are formed. — HOMER ADKINS.

[29] FITTIG, *Annalen,* 110, 32 (1859).

[30] LOUISE, *Compt. rend.,* 95, 602 (1882).

[31] WALLACH, *Berichte,* 29, 2955 (1896), *C.,* 1897 (1), 322.

[32] CLAISEN and PONDER, *Annalen,* 223, 139 (1884).

[33] BAEYER and DREWSEN, *Berichte,* 15, 2856 (1882).

[34] CLAISEN and CLAPARÈDE, *Berichte,* 14, 2463 (1881).

[35] CLAISEN, *Berichte,* 20, 657 (1887).

The same aldehyde gives *benzylidene-hydrindone* with *hydrindone* and a little alcoholic potash:

$$C_6H_4 \Big\langle \begin{array}{c} CH_2 \\ CO \end{array} \Big\rangle CH_2 + OCH.C_6H_5 \rightarrow C_6H_4 \Big\langle \begin{array}{c} CH_2 \\ CO \end{array} \Big\rangle C : CH.C_6H_5.^{[36]}$$
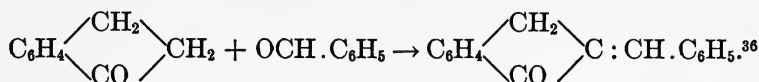
Cinnamic aldehyde, digested several hours with acetophenone in contact with soda, passes into *diphenyl-pentadieneone*:[37]

$$C_6H_5.CH : CH.CH : CH.CO.C_6H_5.$$

Cyclopentanone condenses with two molecules of *benzaldehyde* in contact with soda.[38]

800. *Citral* (50 cc.) and *acetone* (65 cc.) shaken several hours with 1 l. of 4 % baryta water condense to *pseudo-ionone*.[39]

Condensations in Gaseous Phase

801. Catalytic dehydrating oxides can cause regular condensations of aldehydes or ketones in vapor phase.

The vapors of *acetaldehyde*, or of *paraldehyde*, passed over *thoria* at about 260° yield, along with a mixture of methane and carbon monoxide resulting from the decomposition of the aldehyde, a liquid containing water, *crotonic* aldehyde, *hexadienal*, without doubt associated with a certain amount of *octatrieneal*. Careful hydrogenation of the liquid over nickel at 180°, gives essentially a mixture of normal butyl and hexyl alcohols.[40]

The vapors of *acetone* passed over *thoria* at 410–20° give considerable *mesityl oxide*.[41]

Elimination of Water from a Single Molecule

802. We have seen (308 and 310) that the presence of certain catalysts permits the addition of a molecule of water to certain doubly unsaturated hydrocarbons, the products usually being aliphatic ketones. The inverse reaction, the formation of a doubly unsaturated hydrocarbon by the abstraction of a molecule of water from a ketone, can be realized also. It has been found that the vapor of methyl-isopropyl-ketone, passed, under reduced pressure, over kaolin between

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[36] KIPPING, *J. Chem. Soc.*, **65**, 498 (1894).

[37] SCHOLTZ, *Berichte*, **28**, 1726 (1895).

[38] VORLÄNDER and HOBOHM, *Berichte*, **29**, 1840 (1896).

[39] TIEMANN and KRÜGER, *Berichte*, **26**, 2691 (1893). — *Bull. Soc. Chim.* (3), **9,** 798 (1893).

[40] SABATIER and GAUDION, *Compt. rend.*, **166**, 632 (1918).

[41] MAILHE and DE GODON, *Bull. Soc. Chim.* (4), **21**, 63 (1917).

400 and 600°, gives isoprene (which doubtless results from the isomerization of 3-methyl-butadiene (1,2)).[42] We would have:

$$CH_3 . CO . CH{\Large\diagup}^{CH_3}_{\diagdown CH_3} \rightarrow H_2O + CH_2 : C : C{\Large\diagup}^{CH_3}_{\diagdown CH_3} \rightarrow CH_2 : CH . C{\Large\diagup}^{CH_2}_{\diagdown CH_3} .$$
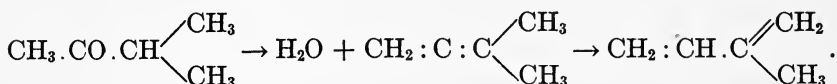
Condensations of Aldehydes or Ketones with Various Organic Molecules

803. Condensations with elimination of water comparable to crotonizations can frequently take place between aldehydes or ketones and molecules of various kinds, nitro compounds, phenols, esters, indols, pyrrols, etc. These reactions are most frequently brought about by the usual condensing agents, *sulphuric or hydrochloric acids, zinc chloride*, etc., or *ammonia* and *amines*, or *anhydrous aluminum chloride*. The products are generally unsaturated at the point where the aldehyde or ketone groups have disappeared.

Thus benzaldehyde condenses with nitromethane in the presence of *zinc chloride* to give a nitro derivative of phenyl-ethylene: [43]

$$C_6H_5 . CHO + CH_3NO_2 = H_2O + C_6H_5 . CH : CH . NO_2.$$

804. The same aldehyde condenses with *malonic acid* or its esters to form *benzylidene-malonic* acid when heated in presence of alcoholic *ammonia* or of *hydrochloric* acid: [44]

$$C_6H_5 . CHO + H_2C (CO_2R)_2 = H_2O + C_6H_5 . CH : C (CO_2R)_2$$
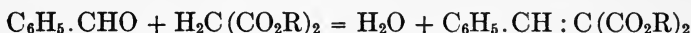
From equal molecules of benzaldehyde and malonic acid warmed 1.5 hours to 55° with an 8 % alcoholic ammonia solution, a 60 % yield of the condensed acid is obtained. The ammonia can be replaced by *ethyl-amine* or *piperidine*.[45]

805. Acetone condenses with *pyrrol* on the addition of a few drops of concentrated *hydrochloric* acid to give a crystalline product, the molecule of which is doubtless quadruple the formula given:

$$C_4H_4N + CH_3 . CO . CH_3 = H_2O + C_7H_9N.$$

[42] EARLE and KYRIAKIDES, *U. S. Patent*, 1,106,290. — *J. Soc. Chem. Ind.*, **33**, 942 (1914).

[43] PRIEBS, *Annalen*, **225**, 321 (1884).

[44] CLAISEN, *Berichte*, **14**, 348 (1881).

[45] KNOEVENAGEL *German patents*, 94,132, 97,735 and 164,296 (1904).

With 1 cc. hydrochloric acid, 14 g. pyrrol and 14 g. acetone dissolved in 80 cc. alcohol and heated, the yield is about 95 %.[46]

806. Trioxymethylene can condense with *benzene* or its homologs in presence of anhydrous *aluminum chloride* to give at the same time *diphenyl-methane* (or a homolog) and anthracene :[47]

$$4C_6H_6 + (CH_2O)_3 = C_6H_5.CH_2.C_6H_5 + C_{14}H_{10} + 3H_2O + H_2.$$
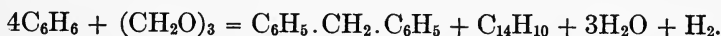
Chloral and *bromal* can react in the same way in the presence of anhydrous aluminum chloride on various aromatic compounds with the elimination of water and the loss of the aldehyde function. This takes place with *benzene* and its homologs :

$$2C_6H_6 + CCl_3.CHO = H_2O + CCl_3.CH(C_6H_5)_2.$$

Resorcine (in carbon disulphide solution) gives a similar reaction but with the simultaneous loss of hydrochloric acid :[48]

$$2C_6H_4(OH)_2 + CCl_2CHO = H_2O + HCl + CCl_2 : C[C_6H_3(OH)_2]_2.$$
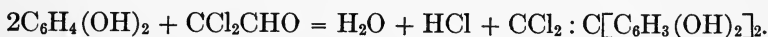
Anisol reacts with chloral to give the compound, $CCl_3.CH-(C_6H_4OCH_3)_2.$[49]

Naphthalene, anthracene, and *phenanthrene* react in an analogous manner with chloral and bromal in the presence of aluminum chloride but with the simultaneous loss of water and halogen hydride. Thus naphthalene gives the compound, $CCl_2 : C(C_{10}H_7)_2.$[50]

§ 14. — ELIMINATION OF WATER BETWEEN ALDEHYDES OR KETONES AND AMMONIA

807. Catalytic oxides can bring about the condensation of aldehydes and ammonia in various ways.

Acetaldehyde and ammonia passed over alumina below 300° give a certain amount of *pyrrol* by simultaneous dehydration and dehydrogenation:[51]

$$\begin{matrix} CH_3.CHO \\ \\ CH_3.CHO \end{matrix} + NH_3 = 2H_2O + H_2 + \begin{matrix} CH:CH \\ | \quad\quad \\ CH:CH \end{matrix}\!\!\!\Big\rangle NH.$$
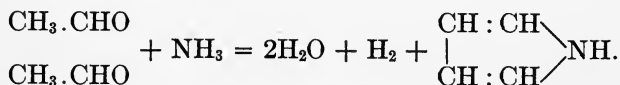
[46] CHELINTZEV and TRUNOV, *J. Russian Phys. Chem. Soc.,* **48,** 105 (1916); *C. A.* **11,** 452 (1917).

[47] FRANKFORTER and KOKATNUR, *J. Amer. Chem. Soc.,* **36,** 1529 (1914).

[48] FRANKFORTER and DANIELS, *J. Amer. Chem. Soc.* **36,** 1511 (1914).

[49] FRANKFORTER and KRITCHEVSKY, *J. Amer. Chem. Soc.,* **37,** 2560 (1915).

[50] FRANKFORTER, *J. Amer. Chem. Soc.,* **37,** 385 (1915).

Acetaldehyde and *benzaldehyde* carried over *alumina* by ammonia at above 300°, yield *α*- and *γ-phenyl-pyridines:* [51]

$$C_6H_5.CHO + 2CH_3.CHO + NH_3 = 2H_2 + 3H_2O + C_5H_4N.C_6H_3.$$

808. Aldehydes and ammonia passed over *thoria* at 420–50° give, by simultaneous dehydration and dehydrogenation, a considerable proportion of *nitriles:*

$$R.CHO + NH_3 = R.CN + H_2O + H_2.$$

With *isovaleric aldehyde,* the yield of nitrile reaches 40 % and equally good results are obtained with *isobutyric, propionic,* and even *benzoic* and *anisic aldehydes.* [52]

809. In contact with thoria at 300–400°, ketones and ammonia give ketimines. With benzophenone the yield is almost theoretical. [53] We have

$$R.CO.R' + NH_3 = H_2O + \begin{matrix} R' \\ \\ R \end{matrix} \!\!\! > C : NH.$$
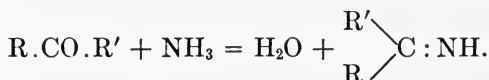
§ 15. — ELIMINATION OF WATER BETWEEN ALDEHYDES AND HYDROGEN SULPHIDE

810. In contact with *alumina* below 300°, *acetaldehyde* condenses with *hydrogen sulphide* with simultaneous dehydration and dehydrogenation to give *thiophene:* [51]

$$2CH_3CHO + H_2S = H_2 + 2H_2O + C_4H_4S$$
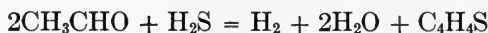
§ 16. — DEHYDRATION OF AMIDES

811. The dehydration of *amides* to *nitriles* can be effected by appropriate catalysts. The amide mixed with the catalyst is heated to 250–60° for 4 hours in a flask fitted with a reflux condenser. Four parts by weight of catalyst are used to one of amide. [54]

Acetamide gave the following yields of *acetonitrile:*

With *alumina*	68 %
lamp black	68
pumice	65
powdered glass.	65
sand	52

[51] Chichibabin, *J. Russian Phys. Chem. Soc.,* **47**, 703 (1915); *C. A.,* **9**, 2512 (1915).
[52] Mailhe and de Godon, *Compt. rend.,* **166**, 215 (1918).
[53] Mignonnac, *Compt. rend.,* **169**, 237 (1919).
[54] Boehner and Andrews, *J. Amer. Chem. Soc.,* **38**, 2503 (1916).

But better yields are obtained by carrying the amide in a current of air over the catalyst heated to 420°, the yields being: [55]

With *pumice* 91.5
    alumina 82
    sand 86.5
    graphite 75.5

812. The same process can be applied to nascent amides furnished by the vapors of the acid with ammonia in excess in the presence of *alumina* or *thoria* at around 500°. Alumina gives the best results. Starting with *acetic acid* an 85 % yield of the nitrile is obtained. [56]

813. We may put along side of the catalytic dehydration of amides to nitriles, the action of *ammonia gas* on the *chlorides* of acids in the presence of catalytic oxides. The amide formed is immediately dehydrated to the nitrile.

The mixture of ammonia and the acid chloride is passed over *alumina* at 490–500° and water and hydrogen chloride are eliminated:

$$R . COCl + NH_3 = R . CN + H_2O + HCl.$$

High yields of the nitriles are obtained in this way from *propionyl*, *isobutyryl*, *isovalyryl* and *benzoyl chlorides*. As the ammonia gas is used in excess, ammonium chloride is formed and deposits in crystals in a receiver placed at the end of the reaction tube. [57]

§ 17. — DEHYDRATION OF OXIMES

814. The *aldoximes* which are isomeric with the *amides* can be transformed into *nitriles* in the same way. The vapors of the aldoximes are passed over *alumina* or *thoria* maintained at 350–60° and give the nitriles. Isovalerald-oxime gave isovalero-nitrile and oenanthald-oxime gave hexyl cyanide. The *ketoximes*, when submitted to the action of these dehydration agents, undergo a complex reaction in which *nitriles* with one less carbon are formed. [58]

§ 18. — DIRECT SULPHONATION OF AROMATIC COMPOUNDS

815. The direct sulphonation of aromatic compounds by means of *concentrated sulphuric acid* corresponds to the elimination of water and can be facilitated or modified by the presence of certain catalysts.

[55] BOEHNER and WARD, *J. Amer. Chem. Soc.*, **38**, 2505 (1916).
[56] VAN EPPS and REID, *J. Amer. Chem. Soc.*, **38**, 2128 (1916).
[57] MAILHE, *Bull. Soc. Chim.* (4), **23**, 380 (1918).
[58] MAILHE and DE GODON, *Bull. Soc. Chim.* (4), **23**, 18 (1918).

The addition of 1 part of *iodine* to 240 parts of benzene warmed with 584 parts sulphuric acid brings about complete sulphonation in 5 hours; the iodine is readily recovered.[59] [60]

816. The catalyst most commonly employed is *mercuric sulphate*.

Benzoic acid heated with sulphuric acid alone gives only the meta and para derivatives, but in the presence of mercuric sulphate, the ortho is obtained.[61]

Anthraquinone gives only the β-monosulphonic acid with sulphuric acid alone, or the 2,6 and 2,7 disulphonic acids, when fuming sulphuric is used.

By heating to 130° with 0.5 part mercury to 110 parts sulphuric acid and 29 parts sulphur trioxide, the α-monosulphonic acid is obtained. At 160° with 1 part mercury to 200 parts sulphuric acid and 40 parts of the trioxide the *disulphonic* acids (1, 5), (1, 6), (1, 7), and (1, 8) are obtained.[62] [63]

Vanadium sulphate has been proposed for aiding the sulphonation of pyridine.[64]

§ 19. — CONDENSATIONS BY ELIMINATING MOLECULES OF ALCOHOLS

817. It is convenient to consider reactions in which molecules of *aliphatic alcohols* are eliminated along with those in which water is abstracted. *Anhydrous aluminum chloride* is specially suitable as a catalyst for such condensations.

Ethyl ether reacts with *benzene* in the presence of aluminum chloride to form *ethyl-benzene* with the elimination of alcohol :[65]

$$C_6H_6 + (C_2H_5)_2O = C_2H_5 . OH + C_6H_5 . C_2H_5.$$

[59] HEINEMANN, *English patent*, 12,260 of 1915. — *J. Soc. Chem. Ind.*, **35**, 1008 (1916).

[60] According to RÂY and DEY (*J. Chem. Soc.* **117**, 1405 (1920)) iodine influences the sulphonation of many compounds notably that of benzoic acid, the sulphonic acid group taking the ortho position under the influence of iodine instead of meta and para: toluene, chlor- and brombenzenes are sulphonated in para position only instead of ortho and para. — E. E. R.

[61] DIMMROTH and VON SCHMAEDEL, *Berichte*, **40**, 2411 (1907).

[62] ILJINSKY, *Berichte*, **36**, 4194 (1914).

[63] In the absence of mercury salts, a very small proportion, about 3 % of α sulphonic acid is formed along with the beta. The presence of the mercury salt does not seem to affect the rate of sulphonation in the beta position but increases the rate of sulphonation in the alpha position so enormously that the operation can be carried on at much lower temperatures and with weaker oleum under which conditions the formation of the β-sulphonic acid is slow. — E. E. R.

[64] FARBW. V. F. BAYER & Co., *German patent*, 160,104.

[1]JANNASCH and BARTELS, *Berichte*, **31**, 1716 (1898).

818. Under the same conditions *benzene* reacts with the *chlormethyl ethers* by the elimination of alcohol to form *benzyl chloride* along with some of the ether $C_6H_5.CH_2.O.R$ (889).   We have:[66]

$$C_6H_6 + ClCH_2.O.R = \underline{ROH} + C_6H_5.CH_2Cl.$$
$$\text{alcohol}$$
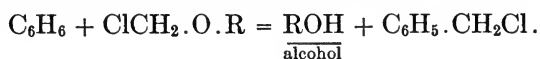
819. **Ethyl nitrate** with *benzene* and aluminum chloride, gives a vigorous reaction which leads to nitrobenzene and the separation of alcohol :[67]

$$C_6H_6 + O_2N.O.C_2H_5 = C_6H_5.NO_2 + C_2H_5.OH.$$
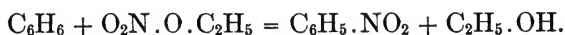
[66] SOMMELET, *Compt. rend.*, **157**, 1443 (1913).
[67] BOEDTKER, *Bull. Soc. Chim.* (4), **3**, 726 (1908).

CHAPTER XVIII

DECOMPOSITION OF ACIDS

820. The aliphatic acids are very stable under the action of heat, except *formic*, which is decomposed by heat under many conditions. We will take up separately the catalytic decomposition of *formic acid* and then the decomposition of other aliphatic and aromatic acids under the influence of metals and of oxides. The action of the oxides leads to important applications which will be studied in succession, the preparation of *symmetrical ketones*, of *mixed ketones* and of *aldehydes*.

DECOMPOSITION OF FORMIC ACID

821. The decomposition of formic acid by heat may go in several distinct directions, either by the separation of *carbon dioxide:*

$$H . CO_2H = CO_2 + H_2 \tag{1}$$

or by the elimination of *water:*

$$H . CO_2H = CO + H_2O \tag{2}$$

or by the simultaneous elimination of water and carbon dioxide from two molecules:

$$2H . CO_2H = \underset{\text{formaldehyde}}{\underline{H . CO . H}} + CO_2 + H_2O. \tag{3}$$
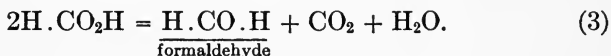
If reactions (1) and (3) coexist, the nascent hydrogen from (1) may sometimes act on the *formaldehyde* produced in (3) to transform it into *methyl alcohol*. We will then have :

$$3H . CO_2H = CH_3 . OH + 2CO_2 + H_2O. \tag{4}$$

The presence of a given catalyst will have the effect of turning the decomposition either into one of these directions or into several at the same time, by lowering more or less the temperature of the decomposition.

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[1] BERTHELOT, *Ann. Chim. Phys.* (4), **18**, 42 (1869). — SAINTE-CLAIRE-DEVILLE and DEBRAY, *Compt. rend.*, **78**, 1782 (1874). — BLACKADDER, *Zeit. phys. Chem.*, **81**, 385 (1912).

822. Reaction (1) which is a dehydrogenation, is produced at the ordinary temperature by *rhodium black*,[1] or by *palladium black*.[2]

Reaction (2) which is a dehydration is brought about by substances that take up water, *sulphuric acid* which acts below 100°, *dry oxalic acid* above 105° or *anhydrous sodium* and *potassium formates* above 150°.[3]

823. Sabatier and Mailhe have studied the decomposition of formic acid under the influence of various catalysts, including *finely divided metals, anhydrous oxides* and some other substances.[4] Comparisons have been made under analogous experimental conditions, the addition of the formic acid being at about 0.27 g. per minute and the pulverulent solid catalyst forming a layer 50 cm. long in a horizontal Jena glass tube heated to a known temperature.

The tube without catalyst gave a negligible decomposition below 300°, while at 340° 2.6 cc. of gas was collected per minute, chiefly a mixture of hydrogen and carbon dioxide (reaction 1) with a few percent of carbon monoxide (reaction 2).

824. The catalysts studied can be divided into three groups:

1st. **Dehydrogenating Catalysts.** These are the ones that cause reaction (1) almost exclusively, doubtless because they give rise to a temporary compound with one of the products, either hydrogen or carbon dioxide. The metals doubtless combine with the hydrogen:

Palladium (sponge) acts at 110° and produces total decomposition at 245°.

Platinum (sponge) begins to decompose it at 120°, the reaction being complete at 215°.

Reduced copper (light violet) evolves at 190° 278 cc. of gas containing equal amounts of hydrogen and carbon dioxide.

Reduced *nickel* at 280° disengages 290 cc. gas containing only traces of carbon monoxide.

Finely divided *cadmium*, prepared by reducing the oxide, gives 325 cc. gas per minute at 280°.

Stannous oxide begins to act above 150°, while at 285° it evolves 172 cc. of gas, being slowly reduced to small globules of *tin* which continue the catalysis. The gas contains a small excess of carbon dioxide due to reaction (3) which takes place to a slight extent.

An analogous result is produced by *zinc oxide* where the temporary production of zinc carbonate is doubtless the cause of the reaction: it begins to act at about 190° and at 230° disengages 172 cc. of gas containing 51 % of carbon dioxide and 49 % of hydrogen by volume.

[2] ZELINSKY and GLINKA, *Berichte*, **44**, 2305 (1911).
[3] LORIN, *Compt. rend.*, **82**, 750 and *Bull Soc. Chim.* (2), **25**, 517 (1876).
[4] SABATIER and MAILHE, *Compt. rend.*, **152**, 1212 (1911).

The production of *formaldehyde* according to equation (3) amounts to 2 %.[5] At 245° this may be raised to 12 % of formaldehyde.[6]

825. 2nd. **Dehydrating Catalysts.** Reaction (2) takes place exclusively with *titania* above 170°, and at 320° 180 cc. of practically pure carbon monoxide is collected per minute.

The *blue oxide of tungsten* (715) acts the same way : at 270° it gives 195 cc. carbon monoxide practically pure.

The reaction goes in the same direction, but with reaction (3) as a side reaction to a slight extent, that is formaldehyde is produced equivalent to the carbon dioxide *without hydrogen*, with *alumina, silica, zirconia,* and *uranous oxide,* UO_2.

With *alumina,* the decomposition, which begins at about 234°, yields carbon monoxide containing 6 % of the dioxide. Reaction (2) dominates but about 10 % is decomposed according to (3) giving *formaldehyde.*

At 340° the disengagement of gas reaches 192 cc. per minute, but the gas then contains a little hydrogen resulting from the partial decomposition of the formaldehyde.

Silica, which is less active than alumina, gives about 3 % of reaction (3).

At 340°, *zirconia* gives 144 cc. gas containing 5 % of carbon dioxide: reaction (3) takes place to an extent of 10 %.

With *uranous oxide,* reaction (3) is almost as important as (2).

826. 3rd. **Mixed Catalysts.** These are the most numerous of all. They produce reactions (1) and (2) simultaneously, usually with (3) as a minor side reaction.

This is what takes place with *thoria.* The decomposition shown by a slight evolution of gas, begins around 230.° It is still quite slow at 250°, and gives a gas which contains 75 % carbon monoxide, 15 % carbon dioxide, and 10 % hydrogen; the condensed liquid contains *formaldehyde.* These figures show that of 100 molecules of formic acid, 79 undergo reaction (2), the other 21 being equally divided between (1) and (3).

Elevation of temperature modifies the conditions of the decomposition which is more and more rapid. At 320° the gas amounts to 120 cc. per minute and the carbon dioxide reaches 45 % and the liquid contains considerable *methyl alcohol,* resulting from the intervention of reaction (4) which may be regarded as a reduction of formic acid by formaldehyde:

$$H.CO_2H + H.CO.H = CO_2 + CH_3.OH.$$

[5] Sabatier and Mailhe, *Compt. rend.,* **152**, 1212 (1911).
[6] Hofmann and Schibsted, *Berichte,* **51**, 1398 (1918).

The amount of *methyl alcohol* increases above 350° and as formaldehyde is then partially decomposed into carbon monoxide and hydrogen, the proportion of hydrogen increases while that of carbon dioxide decreases. At 375°, the gas is 144 cc. per minute containing only 33 % carbon dioxide. The condensate contains methyl alcohol.

827. For certain mixed catalysts, reaction (1) predominates; this is the case with the *blue oxide of molybdenum*, Mo_2O_2, resulting from the reduction of molybdic oxide by the formic acid at 340°. The decomposition, already clean at 105°, gives at 340°, 325 cc. of gas containing only 5 % carbon monoxide. Of 12 molecules of the acid, 9 decompose according to reaction (1), 2 according to (3) and 1 according to (2).

Ferrous oxide, an active catalyst, and *lime* and *broken Jena glass*, mediocre catalysts, favor reaction (1) decidedly.

828. The two reactions (1) and (2) are of about equal importance with powdered white glass which acts at 240°.

The dehydration reaction (2) predominates as is indicated by the proportion of carbon dioxide being less than 33 %, with a large number of substances whose absolute activities differ greatly, thus:

Powdered pumice liberates at 340° . . 4 cc. per minute.
Magnesia 10
Charcoal from light wood 95
Light chromic oxide 150
Black vanadium oxide. 215
Manganous oxide 225
Beryllium oxide 250

Reaction (3) takes place more or less with all of these.

DECOMPOSITION OF MONOBASIC ORGANIC ACIDS

829. In the action of heat on monobasic organic acids we find the three types of reactions given above for formic acid (821), namely:

1st. Elimination of carbon dioxide:

$$R.CO.OH = CO_2 + \underline{\underset{\text{hydrocarbon}}{RH}} \tag{1}$$
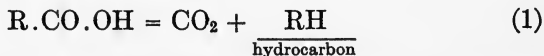
2nd. Separation of water alone, which can take place with primary or secondary acids only:

$$RR'.CH.CO.OH = H_2O + \underline{\underset{\text{ketene}}{RR'C:CO}} \tag{2}$$
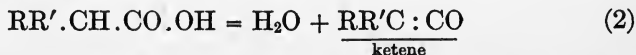
3rd. Simultaneous elimination of water and carbon dioxide from two molecules of acid, giving a symmetrical ketone:

$$2R.CO.OH = CO_2 + H_2O + \underset{\text{ketone}}{R.CO.R} \tag{3}$$
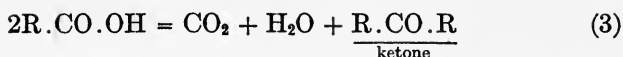
Reaction (2) is realized only *exceptionally*, as in the case of the action of an incandescent platinum spiral on the vapors, not of *acetic* acid but of *acetanhydride*, giving the *ketene*, $CH:CO$,[7] because the ketenes that are formed are very unstable and tend to polymerize ending up with carbonaceous substances.

Reactions (1) and (3) are of great importance.

830. Without the aid of a catalyst these two reactions take place simultaneously at a dull red heat: but the hydrocarbon and even the ketone are more or less destroyed and a complex pyrogenetic mixture results. The presence of a catalyst, either a finely divided metal or an oxide, orients the reaction and lowers the reaction temperature.

With *aliphatic acids*, reaction (1) is the most difficult to effect and is obtained only with difficulty by the use of finely divided metals. On the contrary, reaction (3) is easily brought about by the aid of oxide catalysts and leads to a practical method for the preparation of symmetrical ketones.

Aromatic and *cyclic* acids frequently give reaction (1) under the action of heat alone so that the aid of catalysts is often superfluous. However, the presence of suitably chosen catalysts can either accelerate reaction (1) or substitute for it, partially or entirely, reaction (3) which would not take place in their absence. But among the aromatic acids it is necessary to distinguish between those in which the carboxyl is joined directly to the nucleus and those in which the carboxyl is in a side chain. For the latter, *e.g. phenyl-acetic acid*, $C_6H_5. = CH_2.COOH$, reaction (3) is easily realized by the aid of catalytic oxides as is the case with aliphatic acids.

For the former, *e.g. benzoic*, $C_6H_5.COOH$, and the *toluic acids*, reaction (1) is the one that always tends to take place, reaction (3) being very difficult to obtain, at least with the aromatic acids alone.

SIMPLE ELIMINATION OF CARBON DIOXIDE

831. In the case of *aliphatic acids* this is accomplished more or less by finely divided metals.

Finely *divided copper* commences to decompose the vapors of *acetic acid* at 260°, and an evolution of gas is obtained, slow at first but quite regular at 390–410°, containing 7 volumes of carbon dioxide to 1 of methane. The formation of some acetone is observed. Reactions (1) and (3) are catalyzed and the composition of the gas shows that of 13

[7] WILSMORE, *J. Chem. Soc.*, **91**, 1938 (1901).

molecules of the acid, 1 has decomposed according to reaction (1) and 12 have given acetone.

832. Reduced nickel causes, slowly below 240°, rapidly above 320°, an analogous decomposition. The gas contains 50 % of methane and reaction (1) seems to have taken place exclusively, but a portion of the acids is decomposed into carbonaceous substances which are deposited on the metal.[8]

833. Other aliphatic acids give analogous results. The action of *copper* is slow. That of *nickel* is much more rapid: at 230°, *propionic acid* is broken down into carbon dioxide and ethane which is largely decomposed into methane, carbon and hydrogen. No ketone is formed, but a part of the acid is reduced to the *aldehyde*. At 250°, *butyric acid* gives analogous results, so do *isobutyric* and *caproic*.[9]

834. With *aromatic acids* the decomposition into carbon dioxide and hydrocarbon is usually quite easy.

The vapors of *benzoic acid* carried along by carbon dioxide over reduced copper at 550°, are totally decomposed into benzene and carbon dioxide.

Over nickel, or over the oxide which is rapidly reduced at that temperature, the benzene produced is almost entirely broken up with the deposition of carbon and the liberation of hydrogen and *methane*. Under the same conditions, reduced *iron* gives *benzene*, which is partially destroyed, and some *diphenyl*.[10]

835. In contact with *copper* powder, *coumanic acid* is regularly transformed into γ-*pyrone*:[11]
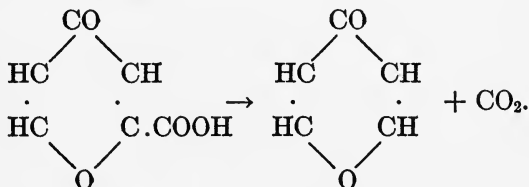
836. The presence of alkaloids favors the decomposition of the carboxy-*camphor* acids at 70° into camphor and carbon dioxide. With an inactive alkaloid, in polarized light, the dextro and laevo acids are decomposed at the same rate; with an active alkaloid, the velocities are different. Thus with quinine a difference of 46 % is found.[12]

The conditions of this decomposition in the presence of quinoline,

[8] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4,** 467 (1905).
[9] MAILHE, *Bull. Soc. Chim.* (4), **5,** 616 (1909).
[10] SABATIER and MAILHE, *Compt. rend.,* **159,** 217 (1914).
[11] WILLSTÄTTER and PUMMERER, *Berichte,* **38,** 1461 (1908).
[12] FAJANS, *Zeit. physik. Chem.,* **73,** 25 (1910).

pyridine, piperidine, and of other amines, benzyl-amine, allyl-, iso-amyl-amine, etc., have been studied in detail, in various solvents at 80° with the result that the formation of a complex by the acid and the amine appears to be the cause of the catalysis in every case.[13]

SIMULTANEOUS ELIMINATION OF WATER AND CARBON DIOXIDE

I. Preparation of Symmetrical Ketones

837. This is the reaction that is specially catalyzed by *metallic oxides*.

It is derived in fact from the old method of preparing symmetrical ketones by calcining at a red heat the calcium or barium salts of mono-basic organic acids:

$$(R.CO_2)_2Ba = R.CO.R + BaCO_3.$$

Squibb conceived the idea of transforming this reaction into a catalytic one. By passing the vapors of *acetic acid* over *barium carbonate* heated to about 500°, a regular and *continuous* decomposition of the acetic acids into *acetone*, water and carbon dioxide is obtained:

$$2CH_3.CO_2H = CH_3.CO.CH_3 + CO_2 + H_2O.$$

The process which gives a yield of better than 90 % has been used industrially. The carbonates of all the metals whose acetates give acetone on calcination may be used.[14] We have studied above (161) the mechanism of this reaction.

838. Ipatief described an analogous formation when he used zinc oxide or *carbonate* or the *carbonates* of *calcium, barium* and *strontium*. Acetic acid gives *acetone*, and propionic acid, *diethyl-ketone*.[15]

839. Calcium Carbonate. This is an excellent catalyst for *acetic acid*, a short column at 450° is sufficient to transform the acid completely into practically pure acetone with the evolution of nothing but carbon dioxide and water.

With *propionic acid*, the yield of *diethyl-ketone* is very satisfactory, some *propionic aldehyde* is obtained and the gas contains a little *ethylene*. This formation of the aldehyde increases with the complexity of the molecule and appears to be correlative to the production of the unsaturated hydrocarbon. We have:

$$C_nH_{2n+1}CO.OH = \underset{\text{hydrocarbon}}{C_nH_{2n}} + \underset{\text{formic acid}}{H.CO.OH}.$$
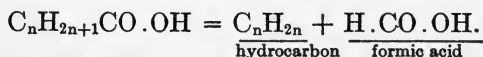
[13] BREDIG and JOYNER, *Zeit. f. Elektrochem.*, **24,** 285 (1918).

[14] SQUIBB, *J. Amer. Chem. Soc.*, **17,** 187 (1895), and **18,** 231 (1896). — CONROY, *Rev. gén. Sci.*, **13,** 563 (1902).

[15] IPATIEF and SCHULMANN, *J. Russian Phys. Chem. Soc.*, **36,** 764 (1904).

The formic acid thus produced can break up at once into $CO_2 + H_2$ or into $CO + H_2O$ (821), but it can act also on the acid that is being used reducing it to the *aldehyde* (851).

The secondary reactions, still more important for *butyric acid*, are exaggerated with *isobutyric* and *isovaleric acids*.

The calcium carbonate used is blackened by the decomposition of a small portion of the acid, but nevertheless conserves its catalytic activity almost indefinitely and remains as carbonate for the most part.[16]

Benzoic acid is scarcely attacked till about 550°, and gives chiefly *benzene* and carbon dioxide with only a little *benzophenone* and traces of *anthraquinone*.[17]

The same difficulty is encountered with the typical aromatic acids in which the carboxyl is united directly to the nucleus, such as *ortho, meta*, and *paratoluic acids* and the *naphthoic acids*.

On the contrary, *aromatic acids* in which the carboxyl is in a side chain, such as *phenyl-acetic*, and *phenyl-propionic* acids can be advantageously transformed into the corresponding symmetrical ketones at 430–70°.

840. Among the metallic oxides the most suitable for the production of ketones are *thoria* and *manganous oxide*. It is sufficient to pass the vapors of the acid over a layer of the oxide, usually below 450°.

Alumina. Alumina gives very good results with *acetic*, not quite so good with *propionic* and quite poor with *isobutyric*.[18] With *benzoic* only a slow decomposition into benzene is effected.

Chromic Oxide. The results are analogous to those obtained with alumina.

Uranium and Zirconium Oxides. These give nearly the same results but their activity diminishes quite rapidly.

Lime. Lime acts as the carbonate. When it is used at 400°, it is possible to observe the formation of the intermediate salt, the decomposition of which furnishes the ketone and which is decomposed only above 420° for the *acetate* and 460° for the *butyrate*. The temperatures reached can account for some decomposition of the ketones formed.

841. **Zinc Oxide.** With zinc oxide, the *acetate* is decomposed above 280° and very rapidly at 340°; the production of acetone is therefore very easy. The difficulty of forming the ketone increases with the molecular weight of the acid and is partly due to the volatility of the zinc salt. *Benzoic acid* is not attacked below 500° and then gives only benzene.

[16] SABATIER and MAILHE, *Bull. Soc. Chim.* (4), **13**, 319 (1913) and *Compt. rend.*, **156**, 1730 (1913).

[17] SABATIER and MAILHE, *Compt. rend.*, **159**, 217 (1914).

[18] SENDERENS, *Bull. Soc. Chim.* (4), **3**, 824 (1908).

842. Cadmium Oxide. This is slowly reduced by the acid vapors but without the activity being diminished by the formation of the metal which can be seen sublimed in the tube. At 400–450° it can readily transform *acetic, propionic, butyric* and *valeric acids* into their symmetrical ketones; the results are not so good with branched chain acids as *isobutyric* and *isovaleric*, with which the gas evolved is no longer pure carbon dioxide but contains considerable amounts of the unsaturated hydrocarbons, carbon monoxide and hydrogen.[19]

It acts at 450°, and violently at 500°, on the vapors of *benzoic* acid to give benzene, the reduction of the oxide hardly modifying the catalysis.[20]

843. Oxides of Iron. *Ferrous oxide* resulting from the calcination of the oxalate as well as *ferric oxide* which is rapidly reduced to the ferrous, can give good results with aliphatic acids at 450–90°. The yield of ketone is excellent with *acetic* or *propionic*, good with *caprylic* and poor with *isobutyric* or *isovaleric* acid.[21]

The immediate formation of a ferrous compound is the basis of a process for the preparation of ketones by heating an acid with 10 % of its weight of iron scale : this works well for the higher fatty acids from *lauric* up to *melissic*. Thus *stearic acid* gives 80 % of the ketone. The results are not so good with *oleïc, elaïdic,* and *brassidic* and are poor with the lower acids, *acetic, butyric,* etc., as well as with *phenyl-acetic, benzoic, suberic,* and *sebacic.*[22]

With *benzoic* acid at 550°, *ferric oxide* acts like *iron* (834), but its simultaneous reduction causes the formation of a certain amount of *phenol* which results from the oxidation of the benzene formed.[23]

844. Thoria. Thoria of which the valuable qualities of constant activity and ready revivification have been mentioned in connection with the dehydration of alcohols (708), gives excellent results with various monobasic aliphatic acids and enables us to prepare with good yields, *acetone, diethyl-ketone, dipropyl-ketone, diisopropyl-ketone, diiso-butyl-ketone, dibutyl-ketone,* etc., as well as ketones derived from aromatic acids in which the carboxyl is not joined immediately to the nucleus, such as *phenyl-acetic, β-phenyl-propionic,* etc.[24]

Benzoic acid is only slowly attacked by thoria even at 550° and then is only decomposed into benzene and carbon dioxide.[25]

[19] MAILHE, *Bull. Soc. Chim.* (4), **13,** 666 (1913).
[20] SABATIER and MAILHE, *Compt. rend.,* **159,** 217 (1914).
[21] MAILHE, *Compt. rend.,* **157,** 219 (1913).
[22] EASTERFIELD and TAYLOR, *J. Chem. Soc.,* **99,** 2298 (1911).
[23] SABATIER and MAILHE, *Compt. rend.,* **159,** 217 (1914).
[24] SENDERENS, *Ann. Chim. Phys.* (8), **18,** 243 (1913).
[25] SABATIER and MAILHE, *Compt. rend.,* **159,** 217 (1914).

845. Manganous Oxide. This oxide prepared by calcining the precipitated carbonate in the vapor of methyl alcohol, is on account of its low price and its great activity, very useful for the preparation of ketones at 400–450°. The carbonaceous deposits do little harm and the same lot of oxide has been used in 22 different preparations. In the case of slightly volatile acids, carbon dioxide is used to carry their vapors along.

The yields of symmetrical ketones are very high, not only for *acetic, propionic* and *valeric acids*, but also for *isobutyric*, with which an experiment carried out at 400–410° gave a 70 % yield, with *caproic, heptoic, nonylic* as well as with *phenyl-acetic*. With *benzoic acid* at 550° a little *benzophenone* is formed, but chiefly *benzene*.[26]

846. Lithium Carbonate. At 550° this is the most advantageous catalyst for transforming *benzoic* acid into *benzophenone*, always accompanied by a little anthraquinone; but even in this, the most favorable case, much benzene is formed.[27]

847. Formation of Ketones in Liquid Medium. In the case of monobasic acids which boil above 300°, the ketones can be formed by heating the acids somewhat above 300° with various catalysts, including the oxides mentioned above, silica, silicates and also finely divided metals. *Stearic acid* yields stearone in 3 hours.[27]

II. Preparation of Mixed Ketones

848. A long time ago Williamson showed that the calcination of a mixture of the calcium salts of two fatty acids gave the mixed ketone:[28]

$$(R.CO_2)_2Ca + (R'.CO_2)_2Ca = 2CaCO_3 + 2R.CO.R'.$$

It might be expected that the catalytic decomposition by means of oxides when applied, not to a single acid but to a mixture of two acids, would give the mixed ketone derived from the two acids instead of the symmetrical ketone. Senderens found this to be the case. We have:

$$R.CO_2H + R'.CO_2H = CO_2 + H_2O + R.CO.R'.$$

A simple method of preparing mixed ketones is to pass a mixture of the vapors of the two acids over thoria at about 400°.

For the success of this method it is sufficient that one of the acids is catalyzed by thoria: we may use two aliphatic acids or one aliphatic with benzoic or a toluic acid, but not benzoic with a toluic.

[26] SABATIER and MAILHE, *Compt. rend.,* **158**, 830 (1914).
[27] SCHICHT ACT. GES. and GRÜN, *German patents*, 295,657 and 296,677. — *J. Soc. Chem. Ind.,* **36**, 569 and 615 (1917).
[28] WILLIAMSON, *Annalen,* **81**, 86 (1852).

The chief reaction is usually that which furnishes the mixed ketone, but it is always accompanied by the reactions that the two acids would undergo separately. We obtain three ketones if we start with two aliphatic acids or an aliphatic and phenyl acetic, but only two when an aliphatic acid is used with benzoic, a toluic, or a naphthoic.

The separation of the ketones is easily accomplished by fractionation. Numerous mixed ketones have been prepared in this way.

849. The *green oxide of uranium*, though less active, can replace thoria for this preparation: *zirconia* acts in the same way, but does not give as good results with the homologs of benzoic acid. *Lime, zinc oxide, alumina,* and *chromic oxide* produce *acetophenone* easily but give poorer and poorer results as the aliphatic acid increases in molecular weight.

Titania, stannic oxide and *ceria* give decomposition products chiefly.[29]

Cadmium oxide, ferrous and *ferric oxides,*[30] and *calcium carbonate* are excellent catalysts for mixed ketones.[31]

850. **Manganous oxide** at 400–450° is as good as thoria and by its use mixed ketones have been prepared from *benzoic acid* with *lauric, myristic,* $C_{14}H_{28}O_2$, and *stearic,* $C_{18}H_{36}O_2$, as well as *phenyl-acetic.*[32]

CATALYTIC PREPARATION OF ALDEHYDES

851. If in Williamson's method for preparing mixed ketones, one of the calcium salts is a formate, an *aldehyde* [33] is produced accompanied by the decomposition products of the individual salts, the symmetrical *ketone,* $R.CO.R$, *formaldehyde,* and *methyl alcohol* as well as gaseous products from the formate:

$$(R.CO_2)_2Ca + (H.CO_2)_2Ca = 2CaCO_3 + \underset{\text{aldehyde}}{\underline{2R.CO.H}}$$
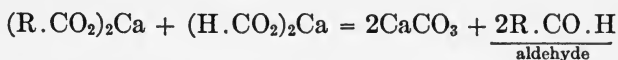
Analogies would lead us to expect that a mixture of the vapors of formic acid and another monobasic organic acid passed over an oxide catalyst would give the aldehyde corresponding to that acid according to the reaction:

$$R.CO_2H + H.CO_2H = R.CO.H + CO_2 + H_2O.$$
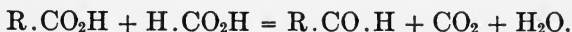
[29] SENDERENS, *Loc. cit.*

[30] MAILHE, *Compt. rend.,* **157**, 219 (1913).

[31] SABATIER and MAILHE, *Compt. rend.,* **156**, 1732 (1913).

[32] SABATIER and MAILHE, *Compt. rend.,* **158**, 830 (1914).

[33] LIMPRICHT, *Annalen,* **97**, 368 (1856). — PIRIA, *Ann. Chim. Phys.* (3), **48**, 113 (1856).

852. Sabatier and Mailhe were able to realize this reaction with *titania* as a catalyst. This constitutes a general method for the preparation of aldehydes from acids. It is sufficient to pass the vapors of the acid mixed with an excess for formic acid over titania heated to 300°. There is evolved a mixture of carbon monoxide resulting from the decomposition of the formic acid by the titania (825) and carbon dioxide from the desired reaction. The condensate is a mixture of water, aldehyde, and unchanged acids from which the aldehyde is easily separated.

Aldehydes derived from various aliphatic acids up to C9 have been thus prepared with yields above 40% and reaching 90%.

Thus *nonylic*, or *pelargonic acid*, gives 85% of *nonylic aldehyde*. Usually no ketone is formed; only very small amounts of the ketones are formed with acids containing more than 5 carbon atoms.

The unsaturated acid, *crotonic*, is likewise transformed into the aldehyde. The reaction gives poor results with *benzoic acid* but works well with phenyl-acetic, the constitution of which is more like the aliphatic acids. It gives a 70% yield.[34]

853. **Manganous oxide** can be substituted for *titania* and has the advantages of being readily prepared and of retaining its activity because it gives rise to less tarry deposits. The operation should be conducted at a little higher temperature, 300–350°. The yields are very satisfactory, reaching 50% with *isovaleric acid*. *Caproic, heptoic, octoic*, and *nonylic aldehydes* have been prepared in this way.[35]

854. The use of *thoria* is less advantageous because it requires a higher temperature and because it favors the formation of ketones which are found with the aldehydes; however, by operating at 270–300°, 25 to 30%, and sometimes more, of the aldehydes are obtained.[34]

DECOMPOSITION OF DIBASIC ACIDS

855. Solid *oxalic acid*, HOOC.COOH, mixed with alumina is decomposed below 100° into water, carbon monoxide and dioxide.[36]

Glycerine mixed with crystallized *oxalic acid* produces a different result: at 100–110° carbon dioxide and *formic acid* are produced:

$$HOOC.COOH = CO_2 + H.CO_2H.$$
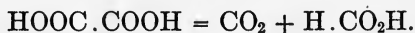
When the reaction dies down all that is necessary to start it again is to add some more oxalic acid and so on, the glycerine being able to

[34] SABATIER and MAILHE, *Compt. rend.*, **154**, 561 (1912).
[35] SABATIER and MAILHE, *Compt. rend.*, **158**, 985 (1914).
[36] SENDERENS, *Bull. Soc. Chim.* (4), **3**, 828 (1908).

serve almost indefinitely, and hence playing the part of a catalyst. In reality there is first the production of a glycerine *mono-oxalate:*

$$HOH_2C.CH(OH).CH_2OH + HOOC.COOH =$$
$$H_2O + HOH_2C.CH(OH).CH_2.CO_2.COOH.$$
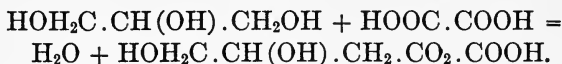
At 100–110° this ester loses water and gives the *monoformine,* $HOH_2C.CH(OH).CH_2.CO_2H$, which is saponified by the water set free in the first reaction liberating formic acid and glycerine which is thus free to recommence the process.

856. The use of *manganous oxide* permits the preparation of *cyclopentanones* from **ε**-*dibasic fatty acids.*

The vapors of *adipic acid* carried along by a current of carbon dioxide over manganous oxide at 350°, give an 85 % yield of *cyclopentanone:*

$$\begin{array}{l} CH_2.CH_2.CO_2H \\ \cdot \\ CH_2.CH_2.CO_2H \end{array} = CO_2 + H_2O + \begin{array}{l} CH_2.CH_2 \\ \cdot \hspace{2em} \diagdown \\ \hspace{3em} \diagup CO. \\ CH_2.CH_2 \end{array}$$
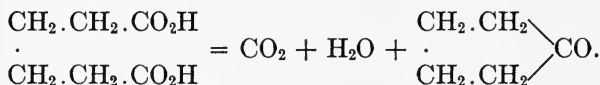
Likewise *β-methyl-cyclopentanone* is prepared from *β-methyl-adipic acid.*[37]

But with *suberic acid,* in which the carboxyl groups are separated by 6 carbon atoms, the process gives only a poor yield of *suberone* and tarry substances are formed which gum up the catalyst.[38]

CATALYTIC DECOMPOSITION OF ACID ANHYDRIDES

857. The anhydrides like the acids can be decomposed catalytically to form the corresponding *symmetrical ketones,* carbon dioxide only being eliminated:

$$R.CO.O.CO.R = CO_2 + R.CO.R.$$

Precipitated *calcium carbonate* gives good results at 450–500° with the *anhydrides* of *acetic, propionic, isovaleric,* etc., *acids. Thoria* is also suitable for this reaction.

This process gives a *mixed ketone* along with the two symmetrical ketones when an acid and the anhydride of another acid are used together.[39]

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[37] SABATIER and MAILHE, *Compt. rend.,* **158**, 985 (1914).

[38] GODCHOT and TABOURY, *Bull. Soc. Chim.* (4), **25**, 352 (1919).

[39] SABATIER and MAILHE, *Bull. Soc. Chim.* (4), **13**, 320 (1913), and *Compt. rend.,* **156**, 1733 (1913).

DECOMPOSITION OF ESTERS OF ORGANIC ACIDS

§ 1. — ESTERS OF MONOBASIC ACIDS

858. In the absence of catalysts the esters of monobasic acids are difficult to decompose by simply heating; the decomposition is slow and such high temperatures are required that the molecules are broken up. We may mention that *ethyl benzoate* heated in a sealed tube above 300° is slowly decomposed into benzoic acid and ethylene. Colson, who noted this reaction and a similar decomposition of *ethyl stearate*, considered this tendency to decompose into the acid and an unsaturated hydrocarbon a general property of esters.[1]

The presence of a catalyst acting at the same time on the alcohols and on the acids should greatly facilitate the decomposition of esters which should yield, in conformity with what has been said above, the unsaturated hydrocarbon and the decomposition products of the acid, water, carbon dioxide, and the symmetrical ketone. Some observations relative to the action of alumina on ethyl acetate, propionate and butyrate confirmed this prediction, but on the contrary, these same esters gave with thoria a complicated decomposition which has not been cleared up.[2]

Sabatier and Mailhe have studied a great number of cases of the action of various catalytic oxides on esters of various sorts and have indicated the general conditions that govern the decomposition.[3]

Formic esters require separate treatment and will be taken up after the other esters.

859. If an ester derived from a primary aliphatic alcohol and from a monobasic organic acid, other than formic, be brought in contact with a catalytic oxide, MO, derived from an amphoteric hydroxide, $M(OH)_2$, the following reaction will take place:

$$2R.CO.OC_nH_{2n+1} + 2MO = (R.COO)_2M + (C_nH_{2n+1}O)_2M.$$
<div style="text-align:center">ester</div>
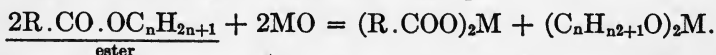
The salt, $(RCO.O)_2M$, and the alcohol derivative, $(C_nH_{2n+1}O)_2M$ are both unstable, if the oxide chosen is at the same time a catalyst

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[1] COLSON, *Compt. rend.*, **147**, 1054 (1908).

[2] SENDERENS, *Bull. Soc. Chim.* (4), **5**, 482 (1909).

[3] SABATIER and MAILHE, *Compt. rend.*, **152**, 669 (1912), and **154**, 49 and 175 (1912).

for the decomposition of alcohols and of acids at the operating temperature.

860. First Case. If the instability of the two temporary compounds is of the same order they will decompose simultaneously and the decomposition becomes:

$$(1) \quad 2R.CO.OC_nH_{2n+1} + 2MO = \left\{ \begin{matrix} \underset{\text{ketone}}{R.CO.R + CO_2} \\ \underset{\text{hydrocarbon}}{2C_nH_{2n} + H_2O} \end{matrix} \right\} + 2MO.$$
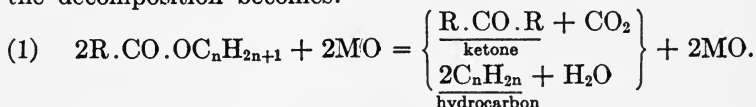
A *symmetrical ketone* is produced and an unsaturated hydrocarbon which, if it is a gas (ethylene, propylene and butylene) has twice the volume of the carbon dioxide produced. This was the case in the experiments with alumina mentioned above (858).

If the ester is a *methyl* ester there is no separation of water, and methyl ether, $(CH_3)_2O$, is formed.

861. Second Case. If the catalyst is more active toward acids than with alcohols, the decomposition of the complex, $(R.CO.O)_2M$, is more rapid than that of the alcohol compound. The water formed in reaction (1) has time to react with an equivalent amount of the latter and decomposes it to regenerate the alcohol:

$$(C_nH_{2n+1}O)_2 + H_2O = MO + \underset{\text{alcohol}}{2C_nH_{2n+1}.OH}.$$
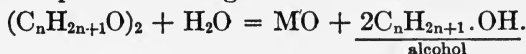
This combined with the former reaction gives:

$$(2) \quad 4R.CO.OC_nH_{2n+1} = \underset{\text{ketone}}{2R.CO.R} + 2CO_2 + 2C_nH_{2n} + 2C_nH_{2n+1}.OH.$$

There is the simultaneous formation of ketone and alcohol and of equal volumes of carbon dioxide and of unsaturated hydrocarbon (if it is a gas). This is usually the case with decompositions caused by thoria, *e.g.* at 310° with *ethyl acetate, propyl acetate, propyl propionate, isobutyl acetate,* and *ethyl caproate.*[4]

[4] Titania prepared by the precipitation of the hydroxide from the sulphate catalyzes the decomposition of ethyl acetate two thirds according to the equation:

(1) $CH_3CO_2C_2H_5 = C_2H_4 + CH_3COOH$

and one third according to:

(2) $2CH_3CO_2C_2H_5 = CH_3COCH_3 + CO_2 + C_2H_4 + H_2O$

Titania prepared by precipitating blue titanous hydroxide from a solution of titanous chloride, and then allowing this to oxidise to the white titanic hydroxide while suspended in the solution, catalyzed the reaction one third according to (1) and two thirds according to (2).

Thoria prepared by ignition of the nitrate gives very little ethylene, as was found by Sabatier, but thoria prepared by precipitation of the hydroxide gives almost as much ethylene as would be called for by (2).

Alumina does not only give reaction (2) but a fifth to two thirds of the ethyl acetate is decomposed according to (1). The method of preparation of the catalyst and the length of time it has been used determine the proportions. — Homer Adkins.

862. Elevation of temperature accelerates the decomposition of the unstable intermediates and tends to bring the reaction nearer to (1). This is the case with *isobutyl acetate* over thoria at above 350° and for *ethyl caproate* at about 360°. Besides when the temperature becomes high, the alcohols suffer more or less decomposition into hydrogen and *aldehydes*, easy to recognize, and these may be partially split up into hydrocarbons and carbon monoxide.

863. **Third Case.** If the catalyst is less active with acids than with alcohols, the temporary complex, $(R.CO.O)_2M$, will be decomposed only slowly. The water set free by the rapid decomposition of the alcohol complex will act on the above to set the acid free:

$$(R.CO.O)_2M + H_2O = MO + \underset{\text{acid}}{2R.CO.OH.}$$
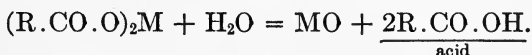
In this case the formation of ketone and liberation of carbon dioxide are less important: the production of unsaturated hydrocarbon and setting free of acid predominate.

This is what takes place over *titania* with esters of acetic, propionic, butyric and valeric acids, which acids it decomposes more slowly than it does the alcohols.

864. **Fourth Case.** The exaggeration of the preceding case is found with those catalysts which are active with alcohols but are incapable of decomposing acids. This is the case with various catalytic oxides, *e.g.* thoria and titania with esters of *benzoic* and *toluic* acids, and with *boric anhydride* with esters of aliphatic acids, since boric acid can form the temporary complexes with the alcohols only. In such cases we may write the reaction as follows:

$$2R.CO.OC_nH_{2n+1} + MO = M(OC_nH_{2n+1})_2 + \underset{\text{anhydride}}{(R.CO)_2O}$$
$$= MO + 2C_nH_{2n} + H_2O + (R.CO)_2O$$
$$= MO + 2C_nH_{2n} + \underset{\text{acid}}{2R.CO_2H.}$$
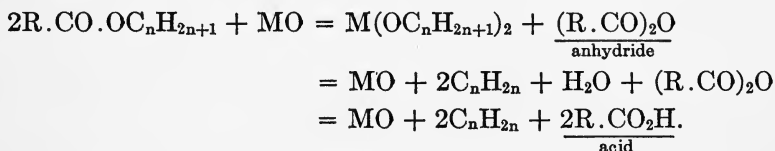
There will be a total regeneration of the acid with the formation of the unsaturated hydrocarbon exclusively. It has been found that *ethyl benzoate* is decomposed into benzoic acid and ethylene by thoria above 400°, as in Colson's sealed tube.

Likewise *ethyl valerate* catalyzed by boric anhydride above 400°, gives ethylene and valeric acid exclusively.

865. **Methyl esters** which can give only methyl ether are difficult to decompose: the reaction, which requires a higher temperature, yields exclusively carbon dioxide, *methyl ether* and the *ketone*, frequently partially decomposed, and resulting water which may saponify a part of the ester to form free acid and methyl alcohol.

Catalytic Decomposition of Formic Esters

866. In the absence of catalysts, formic esters are quite stable: when the vapors of *ethyl formate* are passed through a glass tube at 400°, no appreciable decomposition is observed, but the decomposition is very rapid in contact with catalysts that decompose formic acid (821), and takes place at temperatures lower than those required for the esters of other aliphatic acids, but higher than those required by formic acid.

Sabatier and Mailhe have shown that this decomposition takes place according to two different reactions at the same time, the one similar to the usual decomposition of esters of other aliphatic acids:

$$(1) \qquad 2H.CO_2C_nH_{2n+1} = \underset{\text{formaldehyde}}{\underline{H.CO.H}} + CO_2 + \underset{\text{ether}}{\underline{(C_nH_{2n+1})_2O}}$$
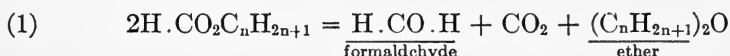
the ether surviving only in the case of methyl ether, splitting in other cases into water and unsaturated hydrocarbon ($H_2O + 2C_nH_{2n}$); the other always predominating, is *peculiar to formic esters:*

$$(2) \qquad H.CO_2C_nH_{2n+1} = CO + \underset{\text{alcohol}}{\underline{C_nH_{2n+1}.OH}}.$$
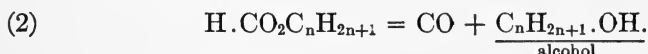
A portion of this alcohol is decomposed at the reaction temperature, either into aldehyde and hydrogen (with metals or manganous oxide), or into unsaturated hydrocarbon and water (with thoria and alumina), or in both ways (with mixed catalysts). The water resulting from reaction (1) or from the dehydration of the alcohol formed according to equation (2) can saponify a part of the ester to alcohol and free *formic acid* which is then decomposed in the way already described (821).[5]

867. **Metals.** Finely divided metals can easily cause the decomposition of formic esters, *nickel* above 220°, *platinum* above 270°, and *copper* above 350°. Reaction (2) greatly predominates and gives the alcohol which the metal breaks down to aldehyde, along with the carbon monoxide. With copper or with nickel at a low temperature the aldehyde survives, but with platinum or with nickel at a high temperature (618) it is largely destroyed.

868. **Titania.** Reaction (2) takes place almost exclusively. From *methyl formate*, methyl alcohol and methyl ether resulting from its partial dehydration are obtained. The gas collected over water is practically pure carbon monoxide without the dioxide because the formic acid, under these conditions, gives only carbon monoxide and water (825).

[5] Sabatier and Mailhe, *Compt. rend.,* **154,** 49 (1912).

869. Zinc Oxide. It is again reaction (2) that predominates, but the formic acid that is set free by the water resulting from the dehydration of the alcohol, is decomposed by the catalyst into water and carbon dioxide which is found mixed with the monoxide.

870. Thoria. Reaction (2) predominates but is accompanied by (1) which furnishes a certain amount of formaldehyde which is diminished as the reaction temperature is raised.

§ 2 — DECOMPOSITION OF ESTERS IN THE PRESENCE OF AMMONIA

871. When the vapors of an ester of an organic monobasic acid mixed with ammonia are passed over *thoria* or *alumina* at about 480–90°, *nitriles* are obtained by the elimination of water and alcohol or of decomposition products of the alcohol.

Methyl esters give the alcohol, partially split into *methyl ether* and water or into *formaldehyde* and hydrogen.

Esters of other aliphatic alcohols give the *unsaturated hydrocarbons*, while *phenol* esters yield *phenol* the major portion of which remains:

$$R.CO.OR' + NH_3 = H_2O + R'OH + RCN.$$
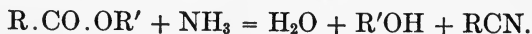
Ethyl acetate gives *ethylene* and *acetonitrile* and *isoamyl acetate* yields *amylene* and *acetonitrile*, while *phenyl acetate* liberates the same nitrile and *phenol*.

Analogous results have been obtained with esters of *propionic, butyric, isovaleric, nonylic* and *caproic acids*.

Methyl benzoate gives more than 80 % of *benzonitrile* with methyl alcohol and formaldehyde. *Ethyl* and *isopropyl benzoates* yield the same nitrile. The esters of the three *toluic acids* behave in the same way.

Ethyl α- and *β-naphthoates* are almost quantitatively transformed into the *α-* and *β-naphthonitriles*.

Ethyl phenyl-acetate gives an excellent yield of benzyl cyanide.[6]

§ 3. — ESTERS OF DIBASIC ACIDS

872. The catalytic decomposition of esters of dibasic acids has been as yet very incompletely studied.

Catalytic oxides such as *alumina* and *thoria* cause decompositions readily. If we extend to the esters of dibasic acids the interpretation above set forth for the action of these oxides, we can predict that an oxide, MO, will effect the reaction:

[6] MAILHE, *Bull. Soc. Chim.* (4), **23,** 232 (1918).

$$(CH_2)_x \Big\langle {\substack{CO.OR \\ CO.OR}} + 2MO = \underbrace{(CH_2)_x \Big\langle {\substack{CO.O \\ CO.O}} \Big\rangle M}_{\text{metal salt}} + \underbrace{M \Big\langle {\substack{OR \\ OR}}}_{\text{alcoholate}}$$

<div align="center">_{ester}</div>

If the oxide is at the same time a catalyst for acids and for alcohols, the compounds thus formed will be unstable and will decompose as follows:

$$(CH_2)_x \Big\langle {\substack{CO.O \\ CO.O}} \Big\rangle M = MO + \underbrace{(CH_2)_x \Big\langle {\substack{CO \\ CO}} \Big\rangle O}_{\text{anhydride}}$$

and:

$$M \Big\langle {\substack{OR \\ OR}} = MO + \underbrace{{\substack{R \\ R}} \Big\rangle O.}_{\text{ether}}$$

The oxide, MO, is entirely regenerated and can carry on the reaction indefinitely. We will obtain as results of the catalysis, the acid *anhydride*, or its debris, if it is unstable, the *ether*, or in most cases, the catalytic decomposition products of that ether, *i.e.* water and an *unsaturated hydrocarbon*.

873. These predictions have been verified by Sabatier and Mailhe in the case of the neutral esters of *oxalic, malonic* and *succinic acids* over thoria.[7]

Oxalic anhydride, ${\substack{CO \\ \cdot \\ CO}} \Big\rangle O$, is unknown and the mixture, $CO_2 +$

CO, is obtained in its place. *Malonic anhydride,* $CH_2 \Big\langle {\substack{CO \\ CO}} \Big\rangle O$, is

equally unstable and decomposes into *carbon suboxide*, CO : C : CO, which polymerizes into reddish products or decomposes into carbon monoxide, dioxide and carbon.

Succinic anhydride is stable if the temperature is not too high and can be collected as crystals melting at 177°. If the temperature is above 350°, it is decomposed into carbon monoxide and dioxide, ethylene and condensation products.

These results have been verified for the *ethyl, propyl, isobutyl* and *isoamyl* esters of the three acids : except in the case of the ethyl esters, where the stable ethyl ether can be collected, the debris of the esters, water and the unsaturated hydrocarbon, are found.[8]

[7] Sabatier and Mailhe, *Bull. Soc. Chim.* (4), **11**, 369 (1912).
[8] Sabatier and Mailhe, *Loc. cit.* and *unpublished results.*

With esters of *oxalic acid*, the catalytic decomposition begins at very moderate temperatures and is already rapid at 220°: higher temperatures are required for *malonates* and still higher for *succinates*.

A decomposition of this nature has been found in the particular case of *ethyl oxalate* over *alumina:* at 200°, ethyl ether, carbon monoxide and dioxide are obtained, while at 360°, the ethyl ether is replaced by ethylene.[9]

874. The catalytic decomposition of *ethyl succinate* over alumina at 400°, according to Senderens, liberated ethylene and carbon dioxide and produced *p. cyclohexadione*.[10] But Sabatier and Mailhe were not able to verify this and obtained only *succinic anhydride* along with ethylene and carbon dioxide. The same results were obtained with alumina at 260°.

Ethyl glutarate over alumina at 270°, gave only ethylene and *glutaric acid*. *Ethyl adipate* furnished ethylene and *adipic acid* at 300°.[11] At higher temperatures this should have given *cyclopentanone* (856).

[9] Senderens, *Bull. Soc. Chim.* (4), **3,** 826 (1908).
[10] Senderens, *Bull. Soc. Chim.* (4), **5,** 485 (1909).
[11] Michiels, *Bull. Soc. Chim. Belge,* **27,** 227 (1913); *C. A.,* **8,** 1106 (1914).

CHAPTER XX

ELIMINATION OF HYDROGEN HALIDES OR SIMILAR MOLECULES

875. THE elimination of hydrogen halides can take place from a single molecule or by condensation from two molecules. Anhydrous chlorides are the chief catalysts in both cases.

§ 1. — ELIMINATION OF HYDROGEN HALIDE FROM A SINGLE MOLECULE

876. When an alkyl *mono-chloride* is passed over a layer of various anhydrous metal chlorides in a tube maintained at above 260° there is rapid decomposition into *unsaturated hydrocarbon* and hydrochloric acid:

$$C_nH_{2n+1}Cl = HCl + C_nH_{2n}.$$

Methyl chloride alone does not decompose in this way.

Barium, nickel, cobalt, lead, cadmium and *ferrous chlorides* are suitable for effecting this reaction. Primary chlorides are decomposed above 260° and rapidly at 300° while secondary and tertiary are still more easily acted on.

The same metal chlorides decompose alkyl *mono-bromides* or *mono-iodides* in the same way to form hydrobromic or hydroiodic acids, but higher temperatures are required.[1]

The recombination of the unsaturated hydrocarbon with the liberated hydrogen halide takes place to a certain extent in the tube beyond the catalytic chloride and may yield a certain amount of secondary or tertiary isomers of the original alkyl halide.

Dry barium chloride gives very good results and can effect this decomposition indefinitely; if it is dissolved in water after long use, there is a small residue of viscous very condensed hydrocarbons with a petroleum odor.

The chlorides of monovalent metals, *silver, sodium,* and *potassium* are inactive.

The process applies to monochlor derivatives of *cyclohexane* and *cyclopentane*. It can succeed with *unsaturated mono-chlorides* and even

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[1] SABATIER and MAILHE, *Compt. rend.,* **141,** 238 (1905).

with *halogenated alcohols* [2] as well as with *dichlorcyclohexane* which is converted to *dihydrobenzene*.[3]

877. **Anhydrous aluminum chloride** acts actively in the same manner, but it has the disadvantage of producing liquid products that hinder the continuation of the catalysis. It has been used to transform *propyl chloride* into *propylene*.[4]

878. The catalysis can be explained by the assumption of an unstable organo-metallic combination derived from the alkyl chloride:

$$C_nH_{2+n+1} . Cl + BaCl_2 = HCl + Cl . Ba . C_nH_{2n} . Cl.$$

The mixed complex thus formed would decompose rapidly to give the unsaturated hydrocarbon:

$$Cl . Ba . C_nH_{2n} . Cl = BaCl_2 + C_2H_{2n}.$$
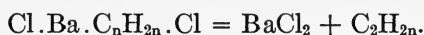
The regenerated chloride can repeat the cycle of reactions indefinitely. The formation of such a mixed complex can be observed in the case of anhydrous *aluminum chloride:* mixed with isobutyl chloride at −10°, no reaction takes place but if the mixture is warmed to 0°, hydrogen chloride and isobutylene are evolved and an intensely colored liquid is formed.

At 300°, *ferric chloride* causes the elimination of hydrogen chloride, but no *isobutylene* is formed; a solid of high molecular weight is produced.

Chromic chloride, $CrCl_3$, does not act.[5]

879. As has been mentioned above (876), this kind of catalysis can be applied to poly-halogen derivatives.

Heptachlorpropane, $CCl_3 . CCl_2 . CHCl_2$, is decomposed above 250° by *cuprous chloride* with the elimination of hydrogen chloride to give *pentachlor-propylene*, $CCl_3 . CCl : CCl_2$ at the same time that a splitting of the molecule yields *chloroform* and *tetrachlorethylene*, C_2Cl_4. *Zinc* and *barium chlorides* have little action.[6] *Aluminum chloride gives* a reaction which is limited by the reverse combination of the chloroform with the tetrachlorethylene (902).

880. **Benzyl chloride** is easily decomposed by various anhydrous chlorides particularly those of barium and nickel, into hydrochloric acid and a very high molecular weight compound of the empyrical formula C_7H_6, previously discovered by Cannizzaro and identical with

[2] BADISCHE, *German patent*, 255,519 (1913).

[3] BADISCHE, *French patent*, 441,203.

[4] KEREZ, *Annalen*, **231**, 306 (1885).

[5] SABATIER and MAILHE, *Compt. rend.*, **141**, 238 (1905).

[6] BOËSEKEN, VAN DER SCHEER and DE VOGT, *Rec. Trav. Chim. Pays-Bas*, **34**, 78 (1915).

that formed by the dehydration of benzyl alcohol (714) [7] and which is perhaps *hexaphenyl-cyclohexane*, $(C_6H_5.CH)_6$. The reaction is:

$$x(C_6H_5.CH_2Cl) = xHCl + (C_6H_5.CH)_x.$$

881. Anhydrous metallic oxides can likewise effect the decomposition of alkyl halides in consequence of the formation of a certain amount of the corresponding chloride. When isobutyl chloride is passed over *alumina* at above 250°, the slight dissociation of the alkyl chloride at that temperature can account for the formation of a little chloride or oxy-chloride of aluminum which starts the catalytic action and the amount of which increases rapidly in consequence of the hydrochloric acid evolved. This is the explanation of the decompositions of alkyl chlorides with alumina that have been described. [8] *Thoria* above 390° has been proposed for the decomposition of *tetrachlorethane* into *trichlorethylene:* there is the simultaneous formation of *carbon hexachloride*, C_6Cl_6. [9]

882. It is probably the formation of nickel chloride also, to which may be attributed the identical catalytic effect of *reduced nickel* on alkyl chlorides in the presence of hydrogen; the decomposition takes place easily above 250°. [10]

§ 2. — CONDENSATIONS EFFECTED BETWEEN MOLECULES WITH ELIMINATION OF HYDROGEN HALIDE

883. Anhydrous aluminum chloride causes condensation with elimination of hydrochloric acid between aromatic hydrocarbons and various alkyl or cyclo-alkyl chlorides and bromides effecting the synthesis of a large number of aromatic compounds. This is the basis of the *Friedel and Crafts synthesis.* [11]

I. Alkylation of Aromatic Hydrocarbons

884. Method of Operating. It is common to use a large well dried flask with a stopper through which passes a very large tube the upper end of which is closed by a stopper and which permits the introduction of the solid aluminum chloride and on the side of which is fused a tube inclined upward and connected with a reflux condenser. The hydrogen chloride which is evolved escapes at the top of this con-

[7] CANNIZZARO, *Annalen*, 92, 114 (1854).

[8] SENDERENS, *Bull. Soc. Chim.* (4), 3, 823 (1908).

[9] CHEM. FABR. BUCKAU, *German patent*, 274,782, *J. Soc. Chem. Ind.*, 33, 807 (1914).

[10] SABATIER and MAILHE, *Compt. rend.*, 138, 407 (1904).

[11] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), 1, 489 (1884).

denser and may be led into a tarred flask of water, the gain in weight of which serves as a means of following the reaction so that it may be stopped when the theoretical amount of this acid has been liberated.

The aromatic hydrocarbon in large excess (usually 10 times the calculated amount) is mixed with the halogen compound with which it is to react and put into the flask which is warmed on the water bath. The well pulverized anhydrous aluminum chloride is added in small portions, 2 to 20 g. at a time. Whenever the evolution of hydrogen chloride dies down a fresh portion of the chloride is added.

If the alkyl halide is a gas (methyl or ethyl chloride), it may be passed into the flask after the addition of a certain amount of aluminum chloride.

When the reaction is considered finished, the flask is cooled and the mixture is poured into a large excess of cold water acidulated with hydrochloric acid; the oily layer is separated, washed and dried and fractionated.

The simplest case is *methyl chloride* with *benzene:*

$$C_6H_6 + CH_3Cl = HCl + \underset{\text{toluene}}{\underline{C_6H_5.CH_3}}.$$
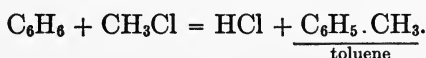
885. Often excellent yields are obtained but the chief product is always accompanied by others, particularly the di- and tri- substituted, resulting from the reaction of the first product with a second molecule of the halide. Thus in the simplest case, that of methyl chloride on benzene, the latter reacts with the toluene that is formed to give a mixture of the *xylenes*. These can react in their turn to yield *trimethyl-benzenes* (1, 2, 4 and 1, 3, 5) and if the reaction is prolonged, *tetramethyl-benzene* (1, 2, 4, 5), then *pentamethyl-* and finally *hexamethyl-benzene* are formed.

By stopping the reaction when the calculated amount of acid has been evolved these complications are avoided for the most part.

The yield of monosubstituted hydrocarbon is considerably increased when an amount of aluminum chloride equal to 15 or 20 % of the weight of the alkyl chloride is used.

The use of carbon disulphide as a solvent sometimes facilitates the reaction.[12]

Alkyl chlorides, bromides or iodides may be used interchangeably, the latter evolving hydrogen bromide and iodide.

886. In place of using aluminum chloride as above described, the flask may be filled with aluminum turnings (previously cleaned by boiling with alcohol and washing with ether) and a current of dry hydro-

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[12] ANSCHÜTZ, *Annalen*, **235**, 207 (1886).

gen chloride passed.[13]   Aluminum turnings may be used with mercuric chloride which attacks the metal rapidly forming the chloride [14]

In some cases the aluminum chloride is put in the flask first and covered with carbon disulphide and then the mixture of the two substances that are to react is run in.

887. Reversal of the Reaction.   The addition of alkyl groups may be limited by the reverse reaction of removing them, and this is also catalyzed by *aluminum chloride.*

When the poly-alkyl benzenes are treated with aluminum chloride and a current of hydrogen chloride, the alkyl side chains are eliminated as alkyl chlorides.[15]   From *hexamethyl-benzene* we may pass to *pentamethyl-*, to *tetramethyl-* (1, 3, 4, 6) and (1, 3, 4, 5) to *trimethyl-* (1, 3, 4) and (1, 3, 5) to *meta* and *para xylenes*, then *toluene* and finally benzene.[16]

888.   It may happen that side chains are taken off of one molecule and put on another in consequence of splitting off an alkyl halide which then reacts with the other molecule.

Thus *poly-ethyl-benzenes* in presence of *benzene* and aluminum chloride, retrograde towards *ethyl-benzene*, particularly in a current of hydrogen chloride which carries off the ethyl chloride.[17]

Ethyl-benzene kept in contact with aluminum chloride furnishes simultaneously *benzene* and *diethyl-benzene*.   Isomerizations may result from an alkyl group being taken off and put on again.   From *p.xylene* we may get *m.xylene* and inversely; *pseudocumene* (1, 3, 4 – tri-methyl-benzene) may give *mesitylene* (1, 3, 5).[18]

889. Results Obtained.   The reaction goes well with various aromatic hydrocarbons, *benzene* and its homologs as well as with *naphthalene* [19] and *diphenyl*.   The homologs of benzene frequently give better results than benzene itself.

It was developed first for *alkyl mono-chlorides* but may go equally well with *cyclohexyl monochlorides: cyclohexyl chloride* and *benzene* give *phenyl-cyclohexane.*[20]

[13] STOCKHAUSEN and GATTERMANN, *Berichte,* **25**, 3521 (1891).

[14] RADZIEWANOWSKI, *Berichte,* **28**, 1135 (1895).

[15] JACOBSEN, *Berichte,* **18**, 339 (1885).

[16] This reaction has been extensively used for the manufacture of toluene from the xylenes. — E. E. R.

[17] RADZIEWANOWSKI, *Berichte,* **27**, 3235 (1894). — BOEDTKER and HALSE, *Bull. Soc. Chim.* (4), **19**, 444 (1916).

[18] ANSCHÜTZ and IMMENDORF, *Berichte,* **17**, 2816 (1884), and **18**, 657 (1885).

[19] It is remarkable that when a solution of naphthalene in benzene is treated with phthalic anhydride in the presence of aluminum chloride, the naphthalene reacts to the exclusion of the benzene. — HELLER and SCHÜLKE, *Berichte,* **41**, 3627 (1908). — E. E. R.

[20] KOURSANOF, *J. Russian Phys. Chem. Soc.*, **33**, 527 (1901); *Bull. Soc. Chim.* (3), **28**, 271 (1902).

It is also applicable to the *chlormethyl ethers*, $R.O.CH_2Cl$, which form the ether $R.O.CH_2R'$ with an aromatic hydrocarbon, $R'H$. With *benzene* the reaction goes regularly in the cold but the yield is only 30%, because *benzyl chloride* is also formed by a side reaction which liberates the alcohol, $R.OH$ (818).[21]

The reaction applies to derivatives of aromatic hydrocarbons which are chlorinated in a side chain, *e.g. benzyl chloride*, $C_6H_5.CH_2Cl$.[22]

Unsaturated monochlorides or monobromides may be used. Thus *vinyl bromide*, $CH_2:CHBr$, condenses with benzene to form *styrene*.[23]

890. **Dihalogen** derivatives may also be used. *Ethylene chloride* reacts with benzene to form symmetrical *diphenyl-ethane*[24] and *1, 1-dibrom-ethylene* forms *1, 1-diphenyl-ethylene*, $CH_2:C(C_6H_5)_2$.[25]

Ethylidene chloride, $CH_3.CHCl_2$, gives similarly *1, 1-diphenyl-ethane*, $CH_3.CH(C_6H_5)_2$, but the reaction may be complicated by the formation of *ethyl-benzene* and *dihydro-dimethyl-anthracene*.[26]

Benzal chloride, $C_6H_5.CHCl_2$, with 5 parts of benzene and a little aluminum chloride, yields *triphenyl-methane*,[27] which may also be formed from benzene and *chloroform*, $CHCl_3$.[28]

II. Synthesis of Ketones

891. The Friedel and Crafts reaction is still more easily applied to the production of *ketones*, by the reaction of aromatic hydrocarbons with *carbonyl chloride*, or with the *chlorides* of *aliphatic* or *aromatic acids*.

Thus carbonyl chloride and benzene form *benzophenone*:

$$COCl_2 + 2C_6H_6 = 2HCl + C_6H_5.CO.C_6H_5.$$

Acetyl chloride produces *acetophenone* from benzene :

$$CH_3.COCl + C_6H_6 = HCl + C_6H_5.CO.CH_3.$$

892. For these preparations equal molecules of the hydrocarbon and the acid chloride are mixed and *carbon disulphide, ligroïne* or *nitrobenzene* is added till a limpid liquid is obtained. Care must be taken to protect from all moisture. This solution is added a little at a time to another flask which contains an equal volume of solvent and

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[21] SOMMELET, *Compt. rend.*, **157**, 1443 (1913).

[22] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), **1**, 478 (1884).

[23] ANSCHÜTZ, *Annalen*, **235**, 231 (1886).

[24] SILVA, *Compt. rend.*, **89**, 606 (1879).

[25] DEMOLE, *Berichte*, **12**, 2245 (1879).

[26] GENVERESSE, *Bull. Soc. Chim.* (2), **49**, 579 (1888).

[27] LINEBURGER, *Amer. Chem. Jour.*, **13**, 270 (1891).

[28] FRIEDEL and CRAFTS, *Bull. Soc. Chim.* (2), **37**, 6 (1882). — E. and O. FISCHER, *Annalen*, **194**, 252 (1878). — ALLEN and KÖLLIKER, *Annalen*, **227**, 107 (1885).

aluminum chloride equal in weight to the acid chloride.[29]   The mixture is warmed slowly on the water bath till no more hydrogen chloride is evolved.

Nitrobenzene as a solvent has the advantage of dissolving aluminum chloride.[30]

The aluminum chloride may be added a little at a time to the mixture of the hydrocarbon and the acid chloride.

893. **Results.** *Acetyl chloride*, $CH_3.COCl$, condenses with *benzene* to form *acetophenone*, $C_6H_5.CO.CH_3$,[31] while *benzoyl chloride*, $C_6H_5.$-$COCl$, gives *benzophenone*, $C_6H_5.CO.C_6H_5$ [32] which may also be obtained by condensing benzene with *carbonyl chloride.* *Benzoyl bromide* may be used with benzene and aluminum bromide.[33]

Chlor- brom-, or nitro- ring substitution products of the aromatic acid chlorides may be used with the same facility.   Thus *m.nitrobenzoyl chloride*, $O_2N.C_6H_4.COCl$, reacts with benzene to form *m.nitrobenzophenone*, $O_2N.C_6H_4.CO.C_6H_5$,[34] and similar compounds can be obtained from the chlor [35] and brom [36] derivatives.

The chlorides of dibasic acids can give a double reaction to form diketones.   Thus *succinyl chloride* and benzene furnish *1, 4-diphenylbutadione (1,4)*, $C_6H_5.CO.CH_2.CH_2.CO.C_6H_5$.   The reaction is carried out in carbon disulphide.[37]

Malonyl and *glutaryl* chlorides react similarly.[38]

On account of its tautomeric nature, *phthalyl chloride* can give different products according to the way the reaction is carried out.
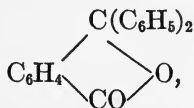
Phthalophenone,[39]   *anthraquinone,*   *diphenyl-anthrone,*[40]

$$C_6H_4 \diagdown \begin{matrix} \diagup C(C_6H_5)_2 \\ \diagdown CO \end{matrix} \diagup O, \qquad C_6H_4 \diagdown \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} \diagup C_6H_4, \qquad C_6H_4 \diagdown \begin{matrix} \diagup C(C_6H_5)_2 \\ \diagdown CO \end{matrix} \diagup C_6H_4$$
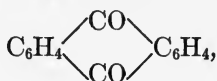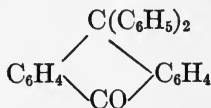
[29] It is better to calculate the amount from its molecular weight and that of the acid chloride; to 1 mol. RCOCl, 1 mol. AlCl₃ = 133.5, is required but 10 % excess is of advantage. — E. E. R.

[30] BEHN, *German patent*, 95,901 (1897).

[31] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), **14,** 455 (1888).

[32] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), **1,** 510, and 518 (1884).

[33] OLIVIER, *Rec. Trav. Chim. Pays-Bas*, **37,** 205 (1918).

[34] GEIGY and KÖNIGS, *Berichte*, **18,** 2401 (1885).

[35] OVERTON, *Berichte*, **26,** 29 (1893). — HANTZSCH, *Berichte*, **24,** 57 (1891). — DEMUTH and DITTRICH, *Berichte*, **23,** 3609 (1890).

[36] CATHCART and MEYER, *Berichte*, **25,** 1498 (1892).

[37] CLAUS, *Berichte*, **20,** 1375 (1887).

[38] AUGER, *Ann. Chim. Phys.* (6), **22,** 349 (1891).

[39] FRIEDEL and CRAFTS, *Ann. Chim. Phys.* (6), **1,** 523 (1884). — BAEYER, *Annalen*, **202,** 51 (1880).

[40] HALLER and GUYOT, *Bull. Soc. Chim.* (3), **17,** 873 (1897).

o.benzoyl-benzoic acid,[41] $C_6H_5.CO.C_6H_4.COOH$, and other products[42] are obtained.

Acid chlorides may react with *pyridine* or *quinoline* in the presence of aluminum chloride to give ketones when traces of *thionyl chloride* are present. From *benzoyl chloride* and *pyridine, pyridyl-phenyl-ketone* is obtained:[43]

$$C_6H_5.CO.Cl + C_5H_5N = HCl + C_6H_5.CO.C_5H_4N.$$
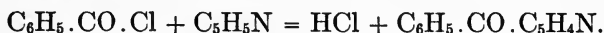
894. Thiophosgene, $CSCl_2$, reacts with aromatic hydrocarbons to form *thioketones:* thus with benzene, *thiobenzophenone,* $C_6H_5.CS.$-C_6H_5.[44]

III. Formation of Amides

895. By the action of carbamic chloride, $Cl.CO.NH_2$, aromatic amides are formed: thus from benzene, benzamide, $C_6H_5.CO.NH_2$ is obtained.[45]

IV. Formation of Cyclic Compounds

896. Methylene chloride condenses with *diphenyl,* $C_6H_5.C_6H_5$, to form fluorene,

$$\begin{matrix} C_6H_4 \\ \cdot \\ C_6H_4 \end{matrix}\Big\rangle CH_2.\ [46]$$
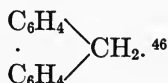
897. Tetrabromethane (1,1,2,2,), or *acetylene tetrabromide*, reacts with *benzene* to form *anthracene:*[47]

$$C_6H_6 + \begin{matrix} BrCHBr \\ \cdot \\ BrCHBr \end{matrix} + C_6H_6 = C_6H_4 \Big\langle \begin{matrix} CH \\ \cdot \\ CH \end{matrix} \Big\rangle C_6H_4 + 4HBr.$$
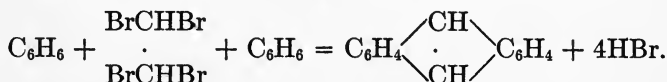
Condensation may take place between two or more molecules of a chlor-compound. Thus *2-phenyl-ethyl chloride,* $C_6H_5.CH_2.CH_2Cl$, reacts vigorously with aluminum chloride in carbon disulphide or ligroïne to form an insoluble resin $(C_6H_4.CH_2CH_2)x$.

Dissolved in 6 parts of ligroïne with 1 part of aluminum chloride, *4-phenyl-butyl chloride* gives an excellent yield of *tetrahydro-naphthalene:*

$$C_6H_4 \begin{matrix} \diagup CH_2.CH_2.CH_2 \\ \qquad \cdot \\ \diagdown H \qquad ClCH_2 \end{matrix} = C_6H_4 \begin{matrix} \diagup CH_2.CH_2 \\ \qquad \cdot \\ \diagdown CH_2.CH_2 \end{matrix} + HCl.$$
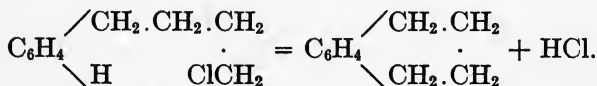
[41] Scheiber, *Annalen*, **389,** 121 (1912).
[42] Copisarow, *J. Chem. Soc.*, **iii,** 10 (1917).
[43] Wolffenstein and Hartwich, *Berichte*, **48,** 2043 (1915).
[44] Bergreen, *Berichte*, **21,** 341 (1888).
[45] Gattermann, *Annalen*, **244,** 29 (1888).
[46] Adam, *Ann. Chim. Phys.* (6), **15,** 253 (1888).
[47] Antschütz, *Annalen*, **235,** 165 (1886).

Similarly *5-phenyl-pentyl chloride* gives *phenyl-cyclopentane* boiling at 213°.[48]

898. Mechanism of the Reaction. We have shown above how the rôle of the aluminum chloride in the Friedel and Crafts reaction may be explained (173). The catalytic nature of the action is not doubted though sometimes it is necessary to employ large amounts of the salt, sometimes larger than the amount of the aromatic hydrocarbon. This is the case when the aluminum chloride combines with one of the products of the reaction and is thus withdrawn from its catalytic function.[49]

899. Other Catalytic Chlorides. Several anhydrous metallic chlorides can be employed in the same way as aluminum chloride in the Friedel and Crafts synthesis: *zinc, ferrous, ferric* and *stannic chlorides* and *antimony pentachloride.*

The use of *ferric chloride* is quite advantageous in preparing ketones.[50] Thus *benzoyl chloride* and benzene give *benzophenone.*[50] Its action, like that of the other chlorides mentioned above, is milder than that of aluminum chloride. For that reason these chlorides sometimes give rise to less formation of byproducts.

For the preparation of benzophenone, the following comparative yields have been obtained:[51]

With *aluminum chloride* . . . . 70–71 %
  ferric chloride 60–62
  zinc chloride 28–32

Aluminum chloride serves poorly for condensing *toluene* with *chlor-methyl ethers* (889), while good results are obtained with *antimony pentachloride* and particularly with *stannic chloride.*[52]

The use of *zinc chloride,* or better metallic zinc which immediately forms some of the chloride, has been recommended for reactions with naphthalene.[53] Thus the *di-naphthyl* ketones are prepared by the action of zinc on a mixture of naphthalene with α- or β-naphthoyl chlorides.[54]

900. A different isomer may be obtained when other chlorides are substituted for the aluminum chloride. *Isobutyl chloride* condensed

[48] von Braun and Deutsch, *Berichte,* **45,** 1267 (1912).

[49] Heller and Schülke, *Berichte,* **41,** 3627 (1908).

[50] Nencki, *Berichte,* **30,** 1766 (1897), and **32,** 2414 (1899). — Meissel, *Berichte,* **32,** 2419 (1899).

[51] Gangloff and Henderson, *J. Amer. Chem. Soc.,* **39,** 1420 (1917).

[52] Sommelet, *Compt. rend.,* **157,** 1443 (1913).

[53] Alexyef, *Méth. de transform. des comb. organ.,* Paris, 1891, 186.

[54] Grucarevic and Merz, *Berichte,* **6,** 1242 (1877).

with toluene in the presence of *ferric chloride* gives *p.methyl-isobutyl-benzene,* while in the presence of aluminum chloride the *meta* compound is obtained.[55]

Formation of Aromatic Amines by Hofmann's Reaction

901. Traces of *cuprous iodide* can readily effect the condensation of primary *aromatic amines* with phenyl bromide, with elimination of hydrobromic acid. The acetyl derivative of the amine may be used. Thus by boiling 90 g. brombenzene, 10 g. acetanilide, 6 g. sodium carbonate and a little cuprous iodide for 15 hours, *acetyl-diphenyl-amine* is obtained and this can readily be transformed into diphenyl-amine. The cuprous iodide can be replaced by copper and iodine or even by copper and potassium iodide.[56]

The presence of *copper powder* greatly facilitates the action of *ammonia* under pressure at 170° on *chlor-nitro-benzene* to form *amino-nitro-benzene.*[57]

It is also useful in the similar reaction of aniline or its homologs on *o.chlor-benzoic* and *2,4-chlor-nitro-benzoic acids* in the preparation of the corresponding amino compounds.[57]

Likewise *pyridine* heated 7 hours to 250° with *benzyl chloride* and a little copper powder gives a good yield of *2-benzyl-* and *4-benzyl-pyridine. Ethyl iodide* and *pyridine* give the *ethyl-pyridines* under the same circumstances. The copper can be replaced by *cuprous chloride. Aluminum* and *magnesium* powders give poorer results.[58]

Condensations in the Aliphatic Series by Anhydrous Chlorides

902. The use of *ferric chloride* enables us to effect important condensations in the aliphatic series. Thus with *propionyl chloride* in the presence of alcohol, two molecules of the acid chloride condense to form the ester of a *keto-acid* :[59]

$$CH_3.CH_2.COCl + CH_3.CH_2.COCl + C_2H_5OH =$$
$$CH_3.CH_2.CO.CH(CH_3).CO_2C_2H_5 + 2HCl.$$
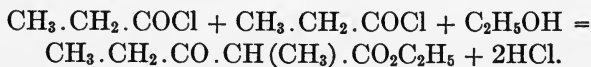
903. **Chloroform** condenses with *pentachlorethane* on contact with aluminum chloride with evolution of hydrogen chloride to form *heptachlor-propane* :[60]

$$CHCl_3 + CCl_3.CHCl_2 = HCl + CHCl_2.CCl_2.CCl_3.$$

[55] BIALOBRZESKI, *Berichte,* **30,** 1773 (1897).
[56] GOLDBERG, *Berichte,* **40,** 4541 (1907).
[57] ULLMANN, *Annalen,* **355,** 312 (1907).
[58] CHICHIBABINE and RYUMSHIN, *J. Russian Phys. Chem. Soc.,* **47,** 1297 (1915).
[59] HAMONET, *Bull. Soc. Chim.* (3), **2,** 334 (1899).
[60] PRINS, *J. prakt. Chem.* (2), **89,** 414 (1914).

§ 3. — ELIMINATION OF A MOLECULE OF AN ALKALINE CHLORIDE, BROMIDE, OR IODIDE

904. The action of the aromatic halogen derivatives, phenyl *chloride*, *bromide*, and *iodide* on the alkali salts of phenol should form *phenyl ether*, but practically the yield is trifling. It becomes very high when the reaction is carried on under pressure at 150° to 200° in the presence of *finely divided* copper as catalyst. The yield reaches 25 % with the chloride, 82 % with the iodide and 78 % with the iodide.

This process may be applied to the formation of ethers of diphenols.[61]

[61] ULLMANN and SPONAGEL, *Annalen*, **360**, 83 (1907).

DECOMPOSITIONS AND CONDENSATIONS
OF HYDROCARBONS

905. The action of high temperature on hydrocarbons is to dissociate the molecules, from which hydrogen tends to separate, at the same time that it produces a greater or less breaking up of the molecules into groups, CH_3, CH_2, and CH which are capable of uniting to form new complex molecules. There result complicated mixtures of varied constitution to which Berthelot has given the name of *pyrogenetic equilibria* which as the temperature rises tend to produce larger and larger proportions of hydrogen and methane along with substances very rich in carbon and very condensed hydrocarbons.

906. The petroleum industry has taken advantage of reactions of this sort in the process known as "*cracking.*" This process, which was accidentally discovered at Newark, N. J., in 1861, consists in carrying petroleum vapors to high temperatures, above a dull red. Along with usable gases, new hydrocarbons are produced which increase the proportion either of *gasoline* or of *heavy oils* as compared with the original oil.

The effect of temperature begins to be felt at about 325° but is not important below a red heat. The presence of catalysts lowers the temperature of these reactions and makes them easier to carry out. The finely divided metals, *copper, iron, cobalt, nickel, platinum, magnesium,* and *aluminum* can be employed and so may the anhydrous oxides, *titania, zinc oxide* and *alumina,* etc.[1]

It is important to know the results of the pyrogenetic decomposition of the hydrocarbons in the absence of catalysts.

From this point of view, benzene, petroleums and the coal tar hydrocarbons known as solvent naphtha have been the most studied.

907. Benzene is hardly affected below 500°, at which it begins to decompose into *diphenyl,* the formation of which increases till it reaches a maximum at 750°. It is accompanied by *diphenyl-benzene:* carbon is deposited and hydrogen set free without any production of *acetylene* or of *naphthalene* below 800°.[2]

[1] ZELINSKI, *J. Russian Phys. Chem. Soc.,* **47,** 1808 (1915).
[2] ZANETTI and EGLOFF, *J. Ind. Eng. Chem.,* **9,** 356 (1917).

908. American *petroleum*, under the action of heat alone, gives increasing amounts of gas from 450° to 875°, while the density of the liquids produced increases also with the temperature. Between 450° and 600°, the products formed contain more *toluene* than *xylene*, more xylene than *benzene*, and neither *naphthalene* nor *anthracene*. At 650° the proportion of benzene is still lower than that of toluene but above that of xylene. From 700° to 850°, benzene is more abundant than toluene and especially than xylene. The formation of naphthalene begins at 750° and that of anthracene at 800° and both increase rapidly with the temperature.

For 100 parts of petroleum thus treated, the benzene in the product reaches its maximum of 4.7 % at 750°, toluene its maximum of 3.1 % at 650°, and xylene its maximum of 1.9 % at 700°. At 800° we have 2 % naphthalene and 0.3 % anthracene. These aromatic hydrocarbons are associated with various aliphatic.[3]

909. **Solvent naphtha** contains considerable amounts of higher hydrocarbons. When it is heated in steel tubes under 11 atmospheres pressure to 500–800°, it yields considerable amounts of lower hydrocarbons. In the product, benzene reaches its maximum of 42.5 % at 800° and toluene its maximum of 39.9 % at 750°. But as the temperature is raised higher and higher the yield of liquid decreases rapidly in consequence of the more abundant production of gaseous products and of materials poor in hydrogen, the real maximum yield based on 100 parts of solvent naphtha is:[4]

Benzene . . . . 15.9 % at 800°.
Toluene . . . . 20.6 % at 750°.

Under the action of a red heat, *pinene* gives a large number of hydrocarbons, both gaseous and liquid, among which have been found *benzene, toluene, m.xylene, naphthalene, anthracene,*[5] *methyl-anthracene* and *phenanthrene.*[6]

By operating at a barely visible red, along with a terpene isomeric with pinene but boiling higher, *isoprene*, C_5H_8, benzene and its homologs, and poly-terpenes are formed.[7]

Action of Catalysts.

910. The presence of catalysts usually enables us to carry out the same reactions at lower temperatures which is more favorable to the preservation of sensitive products that may be formed. Usually

[3] EGLOFF and TWOMEY, *J. Phys. Chem.*, **20,** 121 (1916).
[4] EGLOFF and MOORE, *J. Ind. Eng. Chem.*, **9,** 40 (1917).
[5] BERTHELOT, *Ann. Chim. Phys.* (3), **39,** 5 (1853), and (4), **16,** 165 (1869).
[6] SCHULTZ, *Berichte*, **10,** 114 (1877).
[7] TILDEN, *Ann. Chim. Phys.* (6), **5,** 120 (1885).

nickel and *iron* act violently tending to produce very advanced dehydrogenation with charring more and more intense as the temperature is raised.

911. **Aliphatic Hydrocarbons.** Methane is only slightly attacked by nickel up to 360° but towards 390° the deposition of carbon is appreciable.[8]

The decomposition is not yet rapid at 910° at which *methane* heated 10 minutes in a porcelain tube, without catalyst, gives only 10 % of hydrogen. The presence of *silica* in the tube does not increase the decomposition, but with *lime* the proportion of hydrogen reaches 35 %, with *wood charcoal*, 69 % while with *metallic iron* it is 73 %.[9]

Ethane decomposes slowly above 325° giving carbon, methane and free hydrogen.

Pentane decomposes in an analogous way : at 350–400° methane is produced with intermediate hydrocarbons and carbon is deposited on the nickel.

Lengthening the carbon chain makes these decompositions more easy;[10] but only above 550° and towards 600° are the liquid hydrocarbons such as are found in Pennsylvania petroleum attacked.

912. **Unsaturated Hydrocarbons.** If a current of *ethylene* is passed over reduced nickel heated above 300° the nickel can be seen to swell up into a voluminous black material which finally fills the tube and chokes it up: all the ethylene disappears and a gas is obtained containing *ethane, methane,* and hydrogen. The proportion of ethane is less with higher temperatures of the metal : at a dull red only traces of it are left.

In contact with nickel, ethylene is decomposed into carbon and hydrogen, but the latter is taken up immediately by a portion of the ethylene to form ethane which is more and more broken down to methane at higher temperatures. The nickel is found diffused in the carbon that is formed.[11]

Propylene suffers an analogous destruction but more slowly and without the voluminous swelling of the metal. The decomposition is appreciable at 210° and is clean at 350°. The escaping gas contains propylene, propane, ethylene, ethane, methane and hydrogen.[12]

All other unsaturated hydrocarbons give analogous results, *e.g.* the

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[8] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 435 (1905).

[9] SLATER, *J. Chem. Soc.*, **109**, 160 (1916).

[10] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 435 (1905).

[11] SABATIER and SENDERENS, *Compt. rend.*, **124**, 616 and 1358 (1897).

[12] SABATIER and SENDERENS, *Compt. rend.*, **134**, 1128 (1902).

vapors of *trimethyl-ethylene* give along with a deposit of carbon, the saturated hydrocarbon with the whole series of lower hydrocarbons.

Cobalt acts in a similar manner but less actively than nickel. With *ethylene* at 360° and even at 425° there is slow carbonization without rapid swelling and much ethylene survives.

Iron does not act till above 350° and gives a still slower decomposition.

Platinum (black or sponge) and reduced *copper* do not have any appreciable action on propylene or ethylene.[13]

913. **Acetylene Hydrocarbons.** Similar dehydrogenating actions, but less intense, are exercised by the finely divided metals on the aletylene hydrocarbons, especially *acetylene*. The action can be divided into two entirely distinct kinds, which coexist. One of these is easily observed with platinum or iron, the other particularly with copper, while nickel superimposes the two effects.

914. **First Kind of Reaction.** Pure *acetylene* when heated with platinum to 150°, is rapidly decomposed into carbon and hydrogen : the heat evolved by this decomposition heats the metal to incandescence which accelerates the destruction giving rise to a great carbonaceous swelling, and which causes the polymerization of the remaining acetylene into benzene, styrene, and hydrides of naphthalene and anthracene as in the celebrated synthesis of Berthelot. This phenomenon was observed by Moissan and Moureu;[14] it is complicated by an important consecutive action, which escaped these chemists but which Sabatier and Senderens have studied.[15]

The hydrogen resulting from the decomposition of one portion of the gas can act on another portion, in the presence of platinum, to form *ethylene* and *ethane*. The liquid collected is small in amount and is chiefly benzene. This is the composition by volume of the gases evolved :

Acetylene	66.2 %
Benzene (vapor)	2.8
Ethylene	25.4
Ethane	0.6
Hydrogen	5.0

915. A much greater destructive activity belongs to *reduced iron* (obtained at about 450°) which is raised by acetylene from room temperature to incandescence. If the tube containing the iron is not heated, the reaction almost stops with the local decomposition due to

[13] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4,** 436 (1905).
[14] Moissan and Moureu, *Compt. rend.*, **122**, 1241 (1896).
[15] Sabatier and Senderens, *Compt. rend.*, **131**, 40, 187 and 267 (1900).

the incandescence, the formation of black voluminous carbon in which the iron is disseminated and of brown liquids, almost entirely aromatic. The gases remaining are little but surviving acetylene and hydrogen saturated with benzene vapor. But if the entire iron tube is kept at above 180°, the hydrogenation of the acetylene is carried on by the metal beyond the incandescent portion so that little acetylene is left and the gas is only hydrogen, ethylene and ethane with the vapors of higher hydrocarbons.

916. Second kind of Reaction. This is caused by *copper*.

If a current of acetylene is passed over light *copper* (obtained by reduction at a low temperature) at 180° the copper is seen to turn brown at once and the pressure diminishes greatly on account of the rapid condensation of the acetylene in contact with the metal. Sometimes the current of acetylene which was 20 cc. per minute is entirely taken up for more than 20 minutes and then slowly begins to pass. At this moment the copper is seen to swell rapidly taking on a lighter tint of brown and soon filling the tube so as to stop the flow of gas.

The condensed liquid is a mixture of unsaturated and aromatic hydrocarbons (*benzene, styrene* etc.), the presence of the styrene causing partial solidification after a time.[16] The small amount of gas that passes out contains, with a small amount of acetylene, hydrogen, ethane and particularly the unsaturated hydrocarbons, ethylene, propylene and butylene, which constitute more than two thirds of it.

The copper is found disseminated in the entire brown solid material formed. If a small portion of this is placed as a layer in another tube and heated to 180–250° in a current of acetylene, the material swells up, again filling the tube. One can start anew with a portion of this material and fill another tube. After three or four such swellings, a material is obtained which is no longer changed when heated in acetylene. This is a lighter or darker brown solid which appears under the microscope to be a thick felt of very fine filaments. It is light and fluffy and may be agglomerated into masses resembling tinder. It is a hydrocarbon of the empyrical formula C_7H_6 in which is found diffused a little copper (about 1.5 %) which has caused its formation : this is *cuprene*.[17] Its composition is identical with that of the condensed hydrocarbon formed by the decomposition of *benzyl chloride* by metallic chlorides (880) or by the dehydration of benzyl alcohol (714), and is perhaps *hexaphenyl-cyclohexane*, $C_6H_6(C_6H_5)_6$.[18]

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[16] On account of polymerization of the styrene to a solid. — E. E. R.

[17] SABATIER and SENDERENS, *Bull. Soc. Chim.* (3), **21**, 530 (1899). — *Compt. rend.*, **130**, 250 (1900). — SABATIER, *3rd Congress on Acetylene, Paris*, 1900, 345 and *4th Cong. Applied Chem., Paris*, 1900, **3**, 134.

[18] SABATIER and MAILHE, *Ann. Chim. Phys.* (8), **20**, 298 (1918).

The formation of cuprene is doubtless due to the formation of an unstable acetylide capable of reacting with acetylene to form a new condensed molecule, thus :

$$nC_2H_2 + nCu = nC_2Cu + nH_2$$

and

$$nC_2Cu + 6nC_2H_2 = \underset{\text{cuprene}}{(C_6H_7)_{2n}} + \underset{\text{regenerated}}{nCu.}$$
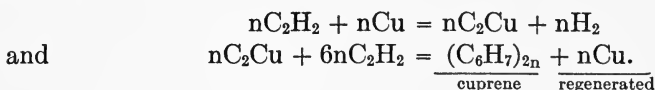
The regenerated metal is capable of repeating the reaction indefinitely. The hydrogen set free combines with a portion of the acetylene over the copper to give chiefly ethylene hydrocarbons.

Compact copper, in sheet or wire, gives a similar formation when heated in acetylene to 200–50° and covers itself with a brown coating which becomes more yellow as its thickness increases.

917. Superposition of the Two Kinds of Reaction. If over a layer of reduced copper heated at its middle portion to above 250° a rapid current of acetylene be passed, incandescence accompanied by intense swelling is observed at this point and there is simultaneous production of *carbon* and of *cuprene* formed by the superposition of the two reactions.

918. Reduced nickel usually causes both reactions. If the reduced nickel is entirely freed from the hydrogen absorbed by its particles, it no longer becomes spontaneously incandescent in acetylene and can be heated to 150° before it causes a reaction. It is only above 180°, that a slow reaction takes place, without incandescence, and this reaction remains thus if the passage of the gas is not too rapid. The metal turns black and swells a little, covering itself with a solid brownish fibrous silky hydrocarbon which suggest *cuprene;* but this formation is slow and if one tries to accelerate it by passing the acelylene more rapidly or by elevating the temperature, incandescence appears bringing rapid decomposition with charring.

Usually when acetylene is passed over a layer of recently reduced, nickel without precautions, there is immediate spontaneous incandescence, brought on by the occluded hydrogen, and carbonizing decomposition takes place always followed by the hydrogenation of the acetylene and of a part of the aromatic hydrocarbons resulting from the incandescence because the nickel is capable of effecting such hydrogenations.

Summing up, nickel acting on acetylene at 180° produces a triple effect :

1st. Rapid decomposition into carbon and hydrogen with polymerization to aromatic hydrocarbons.

2nd. Slow condensation into a solid hydrocarbon doubtless identical with cuprene.

3rd. Hydrogenation of the acetylene and of the aromatic hydro-carbons with production of aliphatic, unsaturated and cyclo-aliphatic hydrocarbons.

With a tube that is not externally heated, where the incandescence is intense and localized at a single point, the first effect is the greatest, the velocity of the gas rendering the subsequent hydrogenation unimportant. These are the conditions studied by Moissan and Moureu.

919. With *cobalt* quite free from nickel and reduced from oxide at below 350°, incandescence is not obtained, starting with the tube cold, but is readily started by heating some point on the tube, and is easily maintained if the tube is heated to 200°. The action is inter-mediate between that of iron and that of nickel. The tube is filled with a black mass consisting of carbon in which the cobalt is diffused and traces of a hydrocarbon analogous to cuprene can be seen.[19]

920. The effects of nickel, iron, cobalt and copper are much less intense when these metals are employed in the form of sheets and have appeared to many observers negligible even up to 600°. On the con-trary *magnesium* powder acting at 600° on methane, ethane, ethylene and acetylene causes a 95 % decomposition. *Aluminum* powder, at near the fusion point of the metal, causes a total decomposition while, *platinum* decomposes only 80 %.[20]

Hexane, under high pressure, is attacked energetically at 650–700° in an iron tube in the presence of *alumina*.[21]

921. **Cyclic Hydrocarbons.** As has been said above (640), the hydro-cyclic hydrocarbons in contact with finely divided metals form the corresponding aromatic hydrocarbons by loss of hydrogen; but the cyclic hydrocarbons, benzene, its homologs, naphthalene, anthra-cene etc. are themselves attacked, and tend to be resolved into CH_2 and CH groups like those furnished by the aliphatic hydrocarbons. Metallic oxides also can catalyze decompositions of this sort.

Finely divided nickel, iron and cobalt act energetically above 400° and especially at a dull red heat, on the hydro-cyclic hydrocarbons, among which are the terpenes, and cause, along with dehydrogenations which take place at lower temperatures (640), decompositions more and more serious as the temperature is raised, and accompanied by carbonaceous deposits which increase at the same time. The charring is less intense with *copper*.

The aromatic hydrocarbons, benzene and its homologs, are much

[19] SABATIER and SENDERENS, *Ann. Chim. Phys.* (8), **4**, 430 (1905).

[20] KUSNETZOW, *Berichte*, **40**, 2871 (1907).

[21] IPATIEF and DOVGELEVICH, *J. Russian Phys. Chem. Soc.*, **43**, 1431 (1911); *C. A.*, **6**, 736 (1912).

less affected by the action of finely divided metals than when they are acted on in the nascent state, that is when they are being formed by the dehydrogenation of cyclohexane or terpene hydrocarbons.

922. The Case of Pinene. The action of heat on pinene when its vapors are passed through a red hot tube has been described above (909). The tube being of iron and sometimes filled with broken pumice or porcelain the peculiar influence of the metal or of the filling may enter into the reaction.

By passing these vapors over very light finely divided copper (59), in a glass tube heated to 600–30°, a rapid evolution of gas of high illuminating power consisting of hydrogen charged with the vapors of lower hydrocarbons, is obtained. By conducting the operation very slowly, 100 cc. of pinene gave 81 cc. of condensate which contained :

$$
\begin{aligned}
&13.3 \text{ cc. passing over below} && 95° \\
&27.0 \text{ cc. passing over from} && 95° \text{ to } 150° \\
&31.4 \text{ cc. passing over from} && 150° \text{ to } 185° \\
&9.3 \text{ cc. passing over above} && 185°.
\end{aligned}
$$

Treatment with sulphuric acid, which dissolves the terpenes and the ethylenic and di-ethylenic hydrocarbons, reduced the volume to 31.5 cc. of hydrocarbons almost entirely nitrifiable and consisting of about 19 cc. cymene and methyl-ethyl-benzene, 10 cc. m. xylene and toluene and a small amount of benzene. In the most volatile portion of the hydrocarbons is found some isoprene, hardly more than 2 cc. The terpenes remaining in the product have no effect on polarized light.

923. Reduced *nickel* acts more violently than copper at 600° and causes intense carbonization in consequence of its destructive action on ethylenic and di-ethylenic hydrocarbons (912). The gas is richer in hydrogen, the liquids condensed are less and contain a considerable proportion of saturated hydrocarbons resulting from the hydrogenating action of the metal on the unsaturated hydrocarbons and unattacked by either sulphuric or nitric acid.[22]

Reactions carried out in the Presence of Hydrogen

924. The decompositions of the hydrocarbons by the metals correspond to an elimination of hydrogen of which a portion is utilized for hydrogenating the fragments. It seemed probable that the presence of hydrogen with the hydrocarbon molecules would stabilize them or would favor the hydrogenation of the fragments resulting from their decomposition. The stabilization is actually realized in the

[22] SABATIER, MAILHE and GAUDION, *Compt. rend.*, **168**, 826 (1919).

case of the cyclohexane hydrocarbons which are preserved to a great
extent (640), in the case of the aromatic hydrocarbons derived from
the terpenes (644).   Hydrogenation carried out at temperatures at
which the hydrocarbons are broken up would necessarily lead to the
hydrogenation of the fragments that would be formed in the absence
of the hydrogen.

925. **Acetylene.**   We have seen (423) that the direct hydrogena-
tion of acetylene, carried out over cold nickel or at a low temperature,
gives ethane accompanied by a certain amount of higher aliphatic
hydrocarbons, both gaseous and *liquid*: the reason for the formation
of these by-products being the breaking up of the molecule HC $\vdots$ CH,
which takes place at near room temperature, thereby liberating the
CH groups which are hydrogenated to methane, CH_4, or to the groups
CH_2 and CH_3, the groups CH_3, CH_2 and CH being able to unite in
various ways to give, in the cold, more or less complex aliphatic hy-
drocarbons.   By operating continuously for 24 hours with nickel
maintained at 200°, Sabatier and Senderens condensed about 20 cc. of
a clear yellow liquid with a splendid fluorescence and an odor quite
similar to that of rectified petroleum.   It began to boil at about 45° and
half of it passed over below 150°, while at 250° there remained a small
quantity of very fluorescent orange yellow liquid, certainly containing
polycyclic hydrocarbons.   The original liquid had a density of 0.791
at 0° and was slightly attacked by the nitro-sulphuric acid mixture
which extracted a small amount of aromatic hydrocarbons.   The re-
maining oil had a density of 0.753 at 0° and was composed almost
entirely of aliphatic hydrocarbons (pentane, hexane, heptane, octane,
nonane, decane, undecane etc.) which were associated in the original
product with unsaturated hydrocarbons, soluble in slightly diluted
sulphuric acid, and with traces of aromatic hydrocarbons.   The com-
position, odor, density and fluorescence class this liquid with *Penn-
sylvania petroleums*.

926. If through a tube containing reduced nickel and kept be-
tween 200 and 300°, a rapid current of pure acetylene is passed, with-
out hydrogen, a lively incandescence is obtained on account of the
decomposition of the acetylene into carbon and hydrogen (918).   A
portion of the acetylene thus carried to a high temperature condenses
to benzene and other aromatic hydrocarbons according to the reaction
discovered by Berthelot; another portion breaks up into CH groups
which can be hydrogenated along with the aromatic hydrocarbons by
the portion of the nickel layer which remains at 200–300°.   In the
receiver is collected a considerable amount of liquid, greenish by re-
flected light, reddish by transmitted, the appearance of which greatly

resembles crude petroleum. If this liquid is hydrogenated directly over nickel at 200° a colorless liquid is obtained which is only slightly attacked by the nitro-sulphuric acid reagent and which, on fractionation, gives a whole series of liquids of densities similar to those of the corresponding fraction of *Caucasian petroleum*. The chief constituents, as in the petroleum fractions, are the *polymethylene* hydrocarbons resulting from the hydrogenation of the aromatic hydrocarbons formed by the incandescence. As in the Caucasian petroleum there are certain amounts of aliphatic hydrocarbons resulting from the hydrogenation of the CH groups which are set free and then reunited in various fashions.

927. By causing incandescence in mixtures of acetylene and hydrogen, the proportion of the aliphatic hydrocarbons is increased and the poly-methylenes diminished and *intermediate petroleums* are obtained.

If the hydrogenation following the incandescence takes place at about 300°, the cyclohexane hydrocarbons are formed only incompletely and are accompanied by certain proportions of untransformed aromatic hydrocarbons : we have *Galician petroleum*.

928. Analogous reaction can be effected by finely divided cobalt and to a certain extent by iron. Sabatier and Senderens, who found out the above facts, have based on them a simple theory of the genesis of *natural petroleum*. There are doubtless far down in the earth's crust large masses of alkaline and alkaline earth metals as well as of the carbides of these metals. Water penetrating through fissures in the rocks and coming in contact with these materials will evolve hydrogen and acetylene, in proportions which will doubtless vary greatly.

If the hydrogen is in large excess, the gaseous mixture, coming in contact with nickel, cobalt or iron disseminated in adjacent rocks at temperatures which may be lower than 200°, gives rise to *American petroleum* and at the same time to large quantities of combustible gases in whch are found, as in the natural gas of the Pittsburgh district, much methane, ethane and free hydrogen.[23]

Use of Anhydrous Aluminum Chloride

929. Anhydrous *aluminum chloride* heated with aliphatic hydrocarbons, tends to decompose them into lower and higher hydrocarbons. *Amylene* gives *methane* at the same time as hexane and still more condensed hydrocarbons.[24]

930. More important and more regular effects are observed with

[23] Sabatier and Senderens, *Ann. Chim. Phys.* (8), **4**, 445 (1905). — Sabatier, *Rev. Mois*, **1**, 257 (1906).

[24] Aschan, *Annalen*, **324**, 1 (1902).

aromatic hydrocarbons, as has been stated above (887), tending to their degradation and building up at the same time. *Ethyl-benzene* heated with aluminum chloride is degraded to benzene, while diethyl-benzene is formed to compensate (888).

A *xylene* (in which the meta predominated) boiled for 5 minutes with 2 % anhydrous aluminum chloride in an apparatus with a mechanical stirrer gave 29 % of hydrocarbons boiling below 135°. Prolonged boiling raised the yield only to 34 %, nor does increasing the amount of the chloride increase it sensibly. Benzene is formed chiefly with a little *toluene.* The proportion of toluene is no better when the operation is carried on under 18 atmospheres pressure.[25]

Cymene heated with a third of its weight of aluminum chloride gives a mixture which contains : 2 % benzene, 42 % toluene, and 7 % xylene (chiefly *meta*) with a little *di-isopropyl-benzene* and *methyl-di-isopropyl-benzene,* increasing the amount of the catalyst increases the amount of the benzene and decreases the toluene.[26]

931. **Naphthalene** heated in an autoclave at 330° under 10 atmospheres pressure, for 20 minutes with 4 % anhydrous aluminum chloride gives, along with a carbonaceous and tarry material, 32 % of a liquid hydrocarbon of which about half is *dihydro-naphthalene* resulting from the hydrogenation of one part of the naphthalene at the expense of another.[27]

Under the action of anhydrous aluminum chloride, *pinene* gives *pentane* and its homologs as well as cyclohexene hydrocarbons.[28]

Application to the Treatment of Petroleums

932. The use of catalysts enables us to improve greatly the operation of cracking (906) for the purpose of increasing the volatile portion of petroleum, since it lowers greatly the temperature at which the reaction takes place thus permitting the survival of molecules resulting from the decomposition which would otherwise be attacked at the higher temperatures.

If over finely divided metals, such as powdered iron or reduced copper, maintained at a temperature between 400° and a dull red, the vapors of a crude petroleum (from any source) or of petroleum previously stripped of its gasoline, there is partial decomposition into a mixture of hydrogen and gaseous hydrocarbons and liquids of which a considerable proportion distils below 150° and may be separated.

[25] F. Fischer and Niggemann, *Berichte,* **49,** 1475 (1916).

[26] Schorger, *J. Amer. Chem. Soc.,* **39,** 2671 (1917).

[27] F. Fischer, *Berichte,* **49,** 252 (1916).

[28] Steinkopf and Freund, *Berichte,* **47,** 411 (1914).

When the residue is again submitted to the action of finely divided metals, a new amount of volatile liquids is formed, and so on.

The gases evolved are quite abundant and are composed of saturated and unsaturated hydrocarbons having high calorific and illuminating power.

Iron has the inconvenience that it causes an abundant deposit of carbon on its surface. Copper causes much less of this but requires a higher temperature, near to 600°; temperatures below 550° give poor results while above 800° there is intense carbonization with diminution of the yield of gasoline.

Thus starting with an American petroleum containing nothing boiling below 150°, by a single passage over copper at 600°, 1 l. gave 225 cc. gasoline boiling below 150°. At the same time 120 l. of gas was evolved with high illuminating power and having a heating power of 15,000 calories per cu. m.

After some time the copper becomes too much fouled with carbonaceous materials and does not have sufficient activity. In order to regenerate it all that is necessary is to pass over it a current of steam which causes the carbon to disappear without altering the metal while producing water gas which may be used for heating the apparatus.

The liquids thus obtained are composed in part of saturated and aromatic hydrocarbons and in part of hydrocarbons containing one or two double bonds. These are oxidisable and polymerizable and have a disagreeable odor. In the experiment cited above their proportion was 40%.

In order to transform them into saturated compounds without disagreeable odors it is sufficient to hydrogenate their vapors in the presence of finely divided metals (particularly reduced nickel) between 150° and 300°. A hydrocarbon is thus obtained that may be used as *gasoline*. Furthermore, the two phases of the process can be combined so as to transform continously a crude petroleum or petroleum residue into gasoline, of which as high as 75% may be obtained.[29]

933. Numerous patents have been taken out for processes of this sort. One proposes to use finely divided metals at 600° under 6 atmospheres pressure.[30]

In another patent, the gas issuing from the catalytic cracking is charged with ammonia and thus modified is used to carry along the vapors of the hydrocarbon over metal oxides which can be reduced to the metal. The nascent hydrogen set free by the decomposition of the ammonia by the metal, saturates the hydrocarbons and diminishes the

[29] SABATIER, *French patent*, 400,141, May, 1909.
[30] HALL, *English patent*, 17,121, of 1913; *J. S. C. I.*, **33**, 1149 (1914).

amount of the carbonaceous deposits. By this process gasoline free from sulphur is obtained even from Mexican petroleum containing 5 % of sulphur.[31]

934. Catalytic oxides (*titania, alumina,* and *zinc oxide*) can also be utilized for such transformations, particularly for changing Russian cyclohexane petroleums into aromatic hydrocarbons (*benzene, toluene* and homologs). A benzine from Baku (98 to 102°) gave 30 % of aromatic hydrocarbons of which over half was *toluene.*

The use of iron retorts is to be avoided on account of the intense carbonization which this metal causes and the rapid deterioration which results therefrom.[32]

935. **Aluminum chloride** enables us to carry out analogous reactions at much lower temperatures (929).

Petroleum freed from water and gasoline is heated 24 to 48 hours with *dry aluminum chloride.* The products obtained are almost entirely saturated and it is unnecessary to treat them with sulphuric acid, washing with soda and then with water being sufficient to get rid of the hydrogen sulphide. The aluminum chloride is regenerated by submitting the residual coke to a current of chlorine at a red heat. The yield of gasoline from Oklahoma petroleum, which gives only 12.5 % by the ordinary cracking process, is raised to 34.8 % by this method.[33]

936. **Iron chlorides,** although less active, may be substituted for the aluminum chloride, and with Russian oils, very poor in gasoline, a certain amount of hydrocarbons passing over from 40° to 140° is obtained. Of this about 35 % is hexane and heptane while the rest is chiefly 7 and 8 carbon cyclic hydrocarbons. Heavy hydrocarbons the consistence of which resembles asphalt, are produced at the same time.[34]

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[31] Valpy and Lucas, *English patent* 20,470 of 1913 and 2,838 of 1914; *J. Soc. Chem. Ind.,* **34,** 71 (1915).

[32] Zelinski, *J. Russian Phys. Chem. Soc.,* **47,** 1807 (1915).

[33] McAfee, *J. Ind. Eng. Chem.,* **7,** 737 (1915).

[34] Pictet and Lerczynska, *Bull. Soc. Chim.* (4), **19** (1916).

SUPPLEMENT TO CHAPTERS XI AND XII

HYDROGENATION OF LIQUID FATS

937. The liquid fats, oils of various origins, contain along with the neutral glycerine esters of the saturated acids, $(C_nH_{2n}O_2,)$ *palmitic, margaric, stearic, arachidic* etc., a considerable proportion of the glycerine esters of the unsaturated acids, either *ethylenic* acids, $(C_nH_{2n-2}O_2,)$ *hypogaïc, oleïc, elaïdic, erucic* etc., or *diethylenic*, $(CH_{2n-4}O_2,)$ as *linoleïc*, or *unsaturated hydroxy* as *ricinoleïc*, or still more unsaturated acids as *linolenic*, $C_{18}H_{30}O_2$ and *clupadonic*, $C_{18}H_{28}O_2$. The unsaturated acids and their glycerine esters have much lower melting points than the corresponding saturated compounds, thus:

Stearic acid,	$C_{18}H_{36}O_2$	. . . . . melts at	71°
Oleïc acid,	$C_{18}H_{34}O_2$	. . . . . melts at	14°
Ricinoleïc acid,	$C_{18}H_{34}O_3$	. . . . . melts at	26°
Linoleïc acid,	$C_{18}H_{32}O_2$	. . . . . melts below	−18°.

Stearine, or glycerine tristearate, melts at 71.5° while *oleïne*, or glycerine trioleate, is liquid at the ordinary temperature. In some cases these unsaturated compounds have disagreeable odors. The presence of *clupadonic acid* is responsible for the repulsive odor of fish oils.

938. The absorption of *iodine* by fats gives an exact measure of the amounts of unsaturated acids that enter into their constitution.

By the term iodine number we mean the amount of iodine absorbed by 100 parts of the fat.[1]

The following table gives the average value of the iodine number for a number of different fats:

Cocoa butter	36	
Mutton or beef tallow	35 to	47
Hog lard	44 to	70
Goose fat	77	
Olive oil	82	
Colza oil	100	

[1] HÜBL, *Dingler's Polytech. J.*, **253**, 281 (1884).

Almond oil. 98
Castor oil 84
Peanut oil 97
Cottonseed oil 109
Sesame oil 108
Poppy seed oil . . . . 133 to 158
Whale oil 127
Cod liver oil . . . . 140 to 180
Linseed oil 180
Clupadonic acid . . . . 365 to 370.

939. By adding hydrogen and thereby transforming unsaturated glycerides into saturated, the bad odors of certain oils (fish and cocoanut) disappear and the melting points are greatly raised.

When applied to the oils themselves, hydrogenation changes them into solid fats, i.e. more and more solid the more the *oleïne* is transformed into *stearine*.

Sabatier and Senderens showed between 1897 and 1902 that hydrogen is easily added to ethylene bonds in the presence of reduced nickel at temperatures below 250° and it was desired to apply this method to the hydrogenation of the liquid fatty acids or to the oils themselves. It is possible by dragging the vapors of *oleïc acid* by a violent current of hydrogen over nickel at 280° to transform it completely into *stearic acid*. A column of *reduced copper* can effect the same reaction at 300° and in this case the hydrogen may be replaced by water gas.[2]

In the patents of Bedford,[3] the fatty material vaporized in hydrogen under *reduced pressure* is hydrogenated while traversing a vertical cylinder filled with nickeled pumice heated to 200°, but the lowering of the pressure of the gas is unfavorable to its fixation.

940. The difficulty of volatilizing the liquid fatty acids and the practical impossibility of volatilizing the oils themselves led to the abandonment of the reaction on the vapors and to attempts to effect it in the liquid material. The patent of Norman of 1903 comprehended hydrogenation of the vapor and of the liquid.[4]

It is to hydrogenation in the liquid medium that almost all of the very numerous patents applying to this important industrial problem relate : more than 200 have been taken out on the choice, preparation and method of using catalysts or for apparatus.

[2] SABATIER, *French patent*, 394,957 (1907).
[3] BEDFORD and WILLIAMS, *English patent*, 9,112 of 1908. — BEDFORD, *U. S. patent*, 949,954 (1910).
[4] NORMAN, *English patent*, 1,515 of 1903.

941. **Catalysts.** *Nickel* is most frequently employed being used alone in the finely divided state as is obtained by the reduction of the oxide with hydrogen, or more commonly incorporated with an inert material intended to disseminate it and to increase the useful surface of contact with the hydrogen and oil. For this purpose have been used nickeled *pumice,*[5] *kieselguhr,* or infusorial earth, impregnated with nickel[6], nickeled *asbestos*[7], and *wood charcoal* impregnated with nickel.[8] The method of incorporating the nickel with the carrier may vary : for example, the nickel is dissolved in sulphuric acid and double its weight of siliceous material is added (pumice, kaolin, asbestos etc.); the metal is precipitated as the carbonate which is calcined to form the oxide which is thus distributed over every fragment of the porous material, and the oxide is reduced by hydrogen at 350°.[9]

942. It has been suggested to use the finely divided nickel formed in the decomposition of *nickel carbonyl* by heat. Finely divided nickel is kept suspended in oil at above 180° and a current of carbon monoxide or of water gas is passed through. This transforms the metal into nickel carbonyl which immediately breaks down into carbon dioxide, carbon and finely divided nickel which remains suspended in the liquid and is ready to realize its hydrogenation at a somewhat higher temperature, around 220–40°.[10] Practically the nickel thus formed may be only 0.1 % of the oil to be hydrogenated.

It has been proposed to impregnate pumice or kieselguhr with *nickel carbonyl* and then heat it to liberate the metal which should be perfectly spread over the porous material : the catalyst thus prepared is incorporated in the oil to be treated without coming in contact with the air.[11]

943. The substitution of *nickel oxides* for metallic nickel has put over against existing patents, other patents which could not be of value if the oxide does not act until after it has been reduced to the metal, as various investigations seem to have established (598).

[5] NORMAN, *English patent,* 1,515 of 1903. — BEDFORD and WILLIAMS, *English patent,* 9,142 of 1908. — ERDMANN, *German patents,* 211,669, *C.,* **1910** (1),1906, and 222,890 (1907), *C. A.,* **4,** 2715 (1910).

[6] KAYSER, *U. S. patents,* 1,004,035 and 1,008,474 (1911), *J. S. C. I.,* **30,** 1266 and 1461 (1911). —WILBUSCHEWITCH, *French patent,* 426,343 (1910), *J. S. C. I.,* **30,** 966 (1911).— CROSSFIELD and MARKEL, *French patent,* 435,249 (1911), *J. S. C.I.,* **3,** 346 (1912).

[7] SCHWOERER, *German patent,* 199,909 (1906)).

[8] ELLIS, *U. S. patent,* 1,060,673, (1913), *C. A.,* **7,** 2132 (1913). — ITTNER, *Mat. grasses.* **1918,** 4964.'

[9] WILBUSCHEWITCH, *English patent,* 15,439 of 1911, *J. S. C. I.,* **30,** 1170 (1911)

[10] SHUKOFF, *German patent,* 241,823 (1910), *C.,* **1912** (1), 175.

[11] SCHICHT, *Mat. grasses,* **1916,** 4634.

This substitution, inspired by the work of Ipatief (584), has been advised by Bedford and Erdman, who believe that the most active catalyst is a sub-oxide such as N_2O,[12] and has been frequently applied to the hydrogenation of oils.[13] [14]

944. Various salts of nickel have been proposed to replace the oxide as catalyst. Nickel *borate* recommended by Schönfeld [15] as being very active, has been found by other chemists absolutely useless unless broken down to the oxide by a temperature of above 260°, the presence of the boric acid appearing to be unfavorable.[16]

The nickel salts of organic acids, *acetate, lactate,* and especially the *formate* have shown themselves useful.[17] The product produced by heating nickel formate in a current of nitrogen has been advised.[18]

945. The other common metals near to nickel, *iron, cobalt* and *copper* have been rarely used although they figure along with nickel in a large number of patents.[19] The same is true of *platinum* on account of its high price which is not compensated for by any special activity.

946. **Palladium** on the contrary, has been recommended as a catalyst for oils in spite of its high cost because of its remarkable activity, 1 part of metal effecting the hydrogenation of 10,000 [20] parts of oil below 100°. It is advantageously employed at about 80° under 2 or 4 atmospheres of hydrogen.[21] It is best to use the palladium precipitated on an inert carrier, either *animal charcoal* or a metallic oxide or

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[12] BEDFORD and ERDMANN, *J. prakt. Chem.* (2), **87,** 425 (1913).

[13] BEDFORD and WILLIAMS, *French patents,* 418,355 (1910); 436,295 (1911); *J. S. C. I.,* **31,** 444 (1912). — *English patent,* 29,612 of 1910, *J. S. C. I.,* **31,** 398 (1912). — *U. S. patent,* 1,026,339 (1912), *J. S. C. I.,* **31,** 593 (1912).— BEDFORD and ERDMANN, *French patent,* 451,155 (1912),— *J. S. C. I.,* **32,** 602 (1913).

[14] The exact comparative experiments of WILLSTÄTTER and WALDSCHMIDT-LEITZ (*Berichte,* **54, 131,** (1921)) go far towards proving that nickel is entirely inactive unless it contains some oxygen. Using 0.2 g. nickel in 20 cc. water with 1 g. sodium cinnamate, no hydrogen was taken up in 1 hour at 60° but the catalyst was activated by shaking with oxygen for 15 minutes. A number of similar experiments are cited. A quantitative experiment showed that the amount of oxygen absorbed by a sample of nickel, exposed to the air, was not weighable yet the nickel was activated by this exposure. — E. E. R.

[15] SCHÖNFELD, *Zeit. f. angew. Chem.,* **27** (2), 601 (1914), *C. A.,* **8,** 3868 (1914).

[16] ERDMANN and RACK, *Zeit. f. angew. Chem.,* **28,** 220 (1915), *C. A.,* **9,** 1255 (1915).

[17] WIMMER and HIGGINS, *French patent,* 441,097 (1912), *J. S. C. I.,* **31,** 826 (1912).

[18] HIGGINS, *Mat. grasses,* **1917,** 4760.

[19] NORMAN, *English patent,* 1,515 of 1903, *J. S. C. I.,* **23,** 26 (1904). — WILBUSCHEWITCH, *French patent,* 426,343 (1910), *J. S. C. I.,* **30,** 966 (1911).

[20] Hydrogenation of cottonseed oil may be carried on at 180° with this proportion of nickel on a carrier. — E. E. R.

[21] DAY, *U. S. patent,* 826,089 (1906), *J. S. C. I.,* **25,** 1035 (1906).

carbonate or magnesium or nickel, the use for this purpose of iron, lead, zinc or aluminum being unfavorable.[22]

The chief disadvantage in the use of palladium is its excessive cost since some loss of metal is inevitable, the cost according to experience amounting to 1.60 francs per 100 kg. oil treated.

947. Life of Catalysts. Certain substances when found in even small amounts in the oils, paralyze the activity of catalysts and do not take long to render them inactive (112). The most to be feared in the hydrogenation of oils are sulphur compounds.

Hydrogen sulphide immediately renders inactive 100 times its weight of nickel and pulverized *sulphur* is half as effective. The action is less rapid with the same proportion of *sodium sulphide*. On the contrary, sulphates, sodium nitrate, and nickel chloride have no harmful effect. Free chlorine kills the nickel instantly.[23] [24]

In contact with fish oil and whale oil the catalyst is quickly killed; the toxic material is fixed by the metal since if a fresh catalyst is added hydrogenation takes place. Consequently a practical method of purification of these oils is to agitate them with a spent catalyst which abstracts the harmful substances.

948. Oils frequently contain free fatty acids which attack the nickel to the detriment of its catalytic activity. Hence it is best to neutralize them by agitation with pulverized *calcium carbonate* or with a small amount of dilute cold *sodium carbonate* solution. The neutral oil thus obtained may be effectively freed from its toxic materials by agitating it hot with freshly precipitated *cupric hydroxide*.[25]

949. The presence of moisture in the oil or in the hydrogen can lead to a certain amount of saponification at the elevated temperature at which the reaction is carried out, hence it is important to avoid the presence of water and to dry the gas before using it, *e.g.*, by refrigeration to $-20°$.[26]

[22] VEREINIGTE CHEM. WERKE, *German patent*, 236,488 (1910), *C. A.*, **5**, 3633 (1911). — *French patents*, 427,729 and 434,927 (1911), *J. S. C. I.*, **30**, 1022 and 31,346 (1912). — *English patent*, 18,642 of 1911, *C. A.*, **7**, 555 (1913).

[23] MOORE, RICHTER, and ARSDEL, *J. Ind. Eng. Chem.*, **9**, 451 (1917).

[24] It is suggested by WILLSTÄTTER and WALDSCHMIDT-LEITZ (*Berichte*, **54**, 127. (1921), that the poisoning of catalysts, by certain substances, at least, may be due to the fact that they deprive the catalysts of their oxygen content and thereby render them inactive. They show that thiophene removes the oxygen from platinum black. In an experiment in which 1.9 g. benzene was being hydrogenated in acetic acid solution by means of 0.5 g. platinum black, 1.5 mg. thiophene was added whereby the activity of the catalyst was completely destroyed. The catalyst recovered 87 % of its original activity by treatment with oxygen for 2 hours. — E. E. R.

[25] ELLIS and WELLS, *Mat. grasses*, **1917**, 4760.

[26] SOC. DE STEARIN. ET SAVON. DE LYON, *French patent*, 485,414 (1917).

950. Nickel catalysts that have been rendered inactive by long use are regenerated by degreasing and treating with nitric acid and calcining the nitrated material thus obtained.

951. **Amount of Catalyst.** The weight of catalyst can vary much according to the work it has to accomplish. The rapidity of the reaction is nearly proportional to the amount of catalyst used. It is usually best not to cut down the amount of the catalyst since it is convenient to shorten the time of the hydrogenation as much as possible. Usually 2 or 3 % of nickel distributed on an inert material is employed. With palladium the amount of catalyst may be much smaller.[27]

952. **Temperatures.** The temperatures most frequently employed for hydrogenations with nickel are around 180° but may sometimes be as low as 150° and are frequently raised to 200–50° especially when the oxide is used.

Much lower temperatures suffice with palladium, usually 80 to 100°.

Elevation of temperature increases the speed of the reaction greatly. In the neighborhood of 170–80° with nickel, raising the temperature 10° increases the velocity about 20 %.[28]

953. **Hydrogen.** The hydrogen for hydrogenations may be prepared electrolytically or may be produced as a by-product in the manufacture of caustic soda.

It can also be obtained by the action of steam on incandescent coke, the *water gas* thus formed, after absorption of the carbon dioxide, being partially liquefied to eliminate the carbon monoxide. But it is more frequently prepared by the decomposition of water by metallic iron, the iron oxide so formed being reduced at a red heat by water gas.

This decomposition can take place at a red heat alternating with the reduction of the iron oxide which is thus formed; but under these conditions it is difficult to avoid the presence of a certain amount of carbon monoxide which it is important not to admit in appreciable amount.

Amounts of 0.25 to 2 % of carbon monoxide produce a serious diminution in the activity of the catalyst; 6 or 8 % prevent any hydrogenation by the nickel either by forming a deposit of carbon which covers the catalyst (614), or because the carbon monoxide turns the catalytic activity of the nickel to its own use in transforming itself

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[27] Good results on cottonseed oil may be obtained with 0.1 % of nickel distributed on 10 parts of carrier. — E. E. R.

[28] MOORE, RICHTER and VAN ARSDEL, *J. Ind. Eng. Chem.*, **9**, 451 (1917). — *Mat. grasses*, **1918**, 5018.

to methane.[29] This toxicity of carbon monoxide is all the more peculiar since *nickel carbonyl* has no harmful effect when it is sent into the oil with the hydrogen, even in large amount, and since the nickel resulting from its decomposition is, up to a certain limit, superior to reduced nickel.[30]

The result is that *water gas* containing about equal volumes of hydrogen and carbon monoxide with a little carbon dioxide and nitrogen, which can give good results with copper as a catalyst (515), is proscribed in the hydrogenation of oils over nickel.

954. According to Bergius, the formation of hydrogen by water and iron can be very advantageously carried out by operating with water kept in the *liquid* form by high pressures. By working under 300 atmospheres at 300–40°, the reaction :

$$3Fe + 4H_2O = 4H_2 + Fe_3O_4.$$

takes place completely and can be greatly accelerated by the presence of sodium chloride or *ferrous chloride* along with metallic copper. Under exactly the same experimental conditions, the amounts of hydrogen evolved per hour were :

Iron and water alone	at 300°	230 cc.
Iron, water and $FeCl_2$	at 300°	1390
Iron, water, $FeCl_2$ and Cu	at 300°	1930
Iron, water, $FeCl_2$ and Cu	at 340°	3450

An apparatus holding 45 l. can produce 102 cu. m. per day. The iron oxide obtained is in fine powder and easy to reduce to metallic iron by water gas.

The hydrogen thus prepared is very pure since the iron carbides and sulphides which are in the iron are not attacked by liquid water. The hydrogen evolved under a pressure of 300 atmospheres can be stored in steel cylinders without further compression.[31]

955. The volume of hydrogen required for hydrogenation varies with the proportion and nature of the unsaturated acids which enter into the composition of the oils.

For pure *oleïc acid* about 79 cu. m. per 100 k. of acid are required while *linoleïc* acid requires twice and *clupadonic acid* four times this amount.

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[29] MAXTED, *Trans. Faraday Soc.*, **13,** 36 (1918).

[30] MAXTED, *Trans. Faraday Soc.*, **13,** 201 (1918).

[31] BERGIUS, *J. Soc. Chem. Ind.*, **32,** 463 (1913). — *German patents*, 254,593 and 286,961.

The corresponding glycerides require somewhat less, about 76 cu. m. for *oleïne*. The amount required by an oil is proportional to its *iodine number; linseed oil* requires 150 cu. m. per 1000 k. [32]

956. Pressure. It is advantageous to operate under pressures higher than atmospheric, the velocity of the hydrogenation being, at least up to a certain limit, proportional to the pressure of the hydrogen. In practice, pressures of 2 to 15 atmospheres are used.

957. Apparatus. A large number of forms of apparatus, many of which differ only in details, have been devised for the hydrogenation of oils. Contrary to the general impression, it is not necessary to agitate the oil and the catalyst very violently with the hydrogen; the agitation should especially have the effect of replacing hydrogenated portions of the oil in contact with the catalyst by portions not yet acted on.

The various forms of apparatus may be divided into four distinct types :

958. First Type. The oil and hydrogen are simultaneously projected on to a catalytic surface.

This is the principle of the apparatus of Erdmann which is composed of a vertical nickel cylinder in the centre of which a vertical concentric terra cotta cylinder covered with a layer of catalyst with a nickel base, turns slowly; the apparatus is heated to 180° and the oil driven by compressed hydrogen is projected onto the surface of the cylinder and runs down after it is acted upon.[33]

959. In the apparatus of Schwoerer designed to hydrogenate oleïc acid, the acid carried along by steam superheated to 250–70° and mixed with hydrogen is projected on to a helicoidal surface covered with nickeled asbestos.[34]

960. The apparatus of Schlinck belongs in this class; it is composed of a centrifuge which turns on a vertical axis in a closed cylinder at the top of which oil and compressed hydrogen are introduced together. The basket of the centrifuge is furnished with asbestos impregnated with catalyst (specially palladium). The oil on account of the rapid rotation, the hydrogen on account of its pressure traverse

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[32] The volume of hydrogen required to saturate any oil is readily calculated from its iodine number. Thus 1 K of oil whose iodine number is 1, requires 882.0 cc., or 1000 K requires 0.8820 cu.m., of hydrogen measured at 0° C. and 760 mm. Hence multiply these figures by the iodine number of the oil in question. 1 K cottonseed oil with iodine number 110 would take 97.02 1. to saturate it completely or 35.28 1. of hydrogen to bring it down to an iodine number of 70. — E. E. R.

[33] ERDMANN, *German patent,* 211,669 (1907), *C. A.,* **3,** 2732.

[34] SCHWOERER, *German patent,* 199,909 (1906).

this layer simultaneously and partially combine. The partially hydrogenated oil runs out at the bottom; the partially expanded hydrogen passes out at the side of the top of the cylinder and is recompressed to be sent into another cylinder along with the partially treated oil. After passing through a sufficient number of cylinders exactly alike the oil is completely hydrogenated.[35]

961. **Second Type.** The oil mixed with the catalyst is atomized in an atmosphere of hydrogen which is kept at a suitable temperature by steam heat.

The apparatus of Wilbuschewitch which seems to have given good results belongs here. It is composed of an autoclave in the form of an elongated vertical cylinder the lower end of which terminates in a 60° cone which is kept at 160°. The oil to which the pulverulent catalyst has previously been added and which is kept mixed by a suitable rotating apparatus, is atomized at the top of the cylinder where the falling droplets encounter an ascending current of hydrogen. This enters at the lower tip of the cone through a circular chamber the top of which is perforated with holes, passes through the oil which has accumlated in the cone, then up the cylinder where it encounters the droplets of oil with the catalyst and passes out at the top of the cylinder to be used again. The partially hydrogenated oil which accumulates in the cone is sent with the catalyst which it carries into a second autoclave like the first where the hydrogenation is carried further and so on into other cylinders till the desired hydrogenation is obtained.[36]

962. **Third Type.** The hydrogen is atomized into oil holding the catalyst in suspension and heated to a known temperature.

This is the principle of one form of apparatus of Ellis, which consists of a conical heating vessel with vertical axis having its apex at the bottom and heated by circulation of high pressure steam in a double jacket. It is filled with oil for two thirds of its height. The catalyst is added through a hole in the top and the hydrogen admitted at the desired pressure is circulated by means of a pump, being drawn from the top and forced in at the bottom of the cone rising through the oil which it agitates and which it hydrogenates thanks to the catalyst which is suspended in it. The passage of the gas is continued till the desired degree of hydrogenation is attained. At this moment a horizontal circular filtering disc which is operated by a rod which occupies the axis of the cone, is lowered till it rests on the walls of the cone near the apex. The oil is filtered through this disc leaving the

[35] Schlinck, *German patent*, 252,320 (1911), *C. A.*, **7**, 910 (1913). — *English patent*, 8,147 of 1911, *C. A.*, 6, 2858 (1912).

[36] Wilbuschewitch, *French patent*, 426,343 (1910), *J. S. C. I.*, **30**, 966 (1911). — *English patent*, 30,014 of 1910, *J. S. C. I.*, **31**, 443 (1912).

catalyst. The apparatus can be charged with a fresh portion of oil which takes up the same catalyst.[37]

963. Fourth Type. A vigorous agitation brings the oil, catalyst and hydrogen together in the same vessel.

Kayser's apparatus consists of an autoclave heated to 150–60° and filled one fourth full of oil mixed with a pulverulent nickel catalyst under hydrogen introduced at the desired pressure. An agitator consisting of six vanes of metal cloth mounted on a metal frame perpendicular to a horizontal axis, can revolve rapidly and thus cause an intimate mixture of gas, oil and solid catalyst.[38]

964. The apparatus of Kimura is very similar.[39] In the apparatus of Woltmann the agitator rotates on a horizontal axis and carries perforated arms through which the hydrogen is sent in under pressure corresponding to the rate of its fixation by the oil.[40]

965. Results. The hydrogenation of oil is carried on in quite a large number of plants, more than 24 in 1916.

It enables us to obtain from oils of very inferior quality, such as whale oil, fatty materials with odors that are not disagreeable, possessing a remarkable consistence along with high melting points. A regulated hydrogenation enables us to prepare at will products intermediate between the oils and the solid fats.

The fixation of 1 % by weight of hydrogen is sufficient to transform *cottonseed* oil and other oils of that class into substances with the consistency of lard. This result may be attained directly by means of hydrogenation of the whole mass of the oil and stopped at the desired hardness, the operation being carried on at as low a temperature as possible so as not to alter the qualities of the oil. But the desired end can be more surely attained by hydrogenating a portion of the oil to the limit and then mixing this with untreated oil to obtain the desired hardness.

966. The table below gives the melting points of the fats obtained by complete hydrogenation of the oils or fats.[41]

[37] ELLIS, *J. Soc. Chem. Ind.*, **31**, 1155 (1912).

[38] KAYSER, *U. S. patents*, 1,004,035 and 1,008,474 (1911), *J. S. C. I.*, **30**, 1266 and 1461 (1911).

[39] KIMURA, *French patent*, 486,621 (1918).

[40] WOLTMAN, *English patent*, 112,293 (1916), *C. A.*, **12**, 1006 (1918).

[41] MANNICH and THIELE, *Mat. grasses*, **1917**, 4676.

	Melting points	
	Hydrogenated oil	Original
Olive oil	70°	6°
Almond oil	72°	−10°
Peanut oil	64.5°	− 3
Sesame oil	63.5°	−5°
Poppy seed oil	70.5°	−18°
Linseed oil	68°	−16°
Codliver oil	68°	−10°
Cocoa butter	64°	23°
Tallow	62°	35°
Lard oil	64°	28°

The iodine number becomes very small in every case.

967. The commercial grades do not correspond to such complete hydrogenation. They exhale a peculiar, very persistent aromatic odor which resists saponification and distillation under reduced pressure.

Such hardened oils are known under the French trade names of *duratol, talgol, candelite* and *synthetic tallow.*

Below are given some of the characteristics of such products, melting point, iodine number and melting point of the fatty acids : [42] [43]

	M.p.	I. No.	M.p. of Acids.
Talgol	35–37°	86.1	38.5°
Talgol extra	42–44°	63.9	45.5°
Candelite	48–50°	10.4	48.5°
Candelite extra	51–52°	10.5	51.8°

968. **Castor oil** which does not solidify till below −18°, gives on careful hydrogenation a very white hard solid which melts above 80° and which is advantageously employed as an electric insulator.

969. The question of the use of deodorized and hardened oils as fats in food has not been completely settled as yet, because we are not altogether certain about the toxicity of the small amounts of nickel which remain in the materials, amounts that are hardly more than 0.000002 % if the oils treated were entirely neutral.

[42] GÄRTH, *Seif. Zeit.*, **39,** 1277 (1912).

[43] According to information obtained from DR. WESSON, hydrogenation is carried on in the United States by about 60 concerns and hydrogenated oils are important constituents in some 92 brands of shortening. Formerly these were regarded as lard substitutes but they have made an independent position for themselves as "vegetable shortening" and have found favor with many who object to lard.

For edible products cottonseed oil is the chief oil that is hydrogenated. The aim is to prepare a product that will not be too hard in winter or too soft in summer. Sometimes the whole of the oil is hydrogenated. The chief products thus made

for the American market are Crisco, Selex, MFB, and Fairco. These melt at 33 to 37° and have iodine numbers running from 76 to 86. By varying the mode of hydrogenation, products with nearly the same melting points but with iodine numbers varying as much as 10 points may be obtained.

By hydrogenating down to an iodine number of 10 to 20 and mixing this very hard fat with untreated cottonseed oil the desired consistency may be obtained with a much higher average iodine number. This is the most common practice as much less hydrogen is required and the fraction of the oil that has to be hydrogenated is small.

The melting points and iodine numbers of some leading brands are as follows:

	Melting Point	Iodine Number
Scoco	44.4	89.2
Snowdrift	44.1	89.3
Armstrong White Cloud	45.8	99.4
Armstrong Bob White	39.2	93.5
Fairbanks Boar's head	41.8	100
Morris Purity	42.0	97.5
P. and G. Flake white	42.8	90.6
P. and G. White flake	47.8	87.4
Swift Jewel	45.5	97.0
Wilson Advance	44.2	96.9
Kream Krisp	45.5	97.0

Highly hydrogenated cottonseed oil is a hard, white, brittle solid and does not become rancid. These properties make it a suitable constituent for prepared cake flours.

Vast amounts of fish oils are hydrogenated to be used in making soaps.

E. E. R.

AUTHOR INDEX

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SUBJECT INDEX

(References are to Paragraphs: a number followed by "n" designates a note.)

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